Società Chimica Italiana

SCI2021

XXVII CONGRESSO NAZIONALE DELLA SOCIETÀ CHIMICA ITALIANA

LA CHIMICA GUIDA LO SVILUPPO SOSTENIBILE

14–23 SETTEMBRE 2021

Sessioni Plenarie – ABC – ANA

BOOK OF ABSTRACTS
XXVII congresso della SCI, 2021

La chimica guida lo sviluppo sostenibile
14-23 settembre 2021

ISBN 978-88-94952-24-7

Benvenuti a SCI2021!

Il Congresso Nazionale della Società Chimica Italiana, giunto alla sua XXVII edizione, si svolgerà in modo virtuale da martedì 14 settembre a giovedì 23 settembre 2021. Come di consueto, sarà un punto di incontro e di confronto per tutto il mondo della chimica in Italia su argomenti di grande attualità.

Il congresso sarà aperto dalla ***plenary lecture*** **del Prof. Stanley Whittingham, premio Nobel per la Chimica 2019**, e prevede interventi di una serie di illustri oratori, fra cui **il premio Nobel per la Chimica 1981, Prof. Roald Hoffmann**. Il congresso si articolerà in sessioni plenarie di interesse generale e sessioni parallele, a cura delle Divisioni della Società Chimica Italiana. Nel pomeriggio di mercoledì 22 settembre sono previsti eventi satellite di interesse industriale, accessibili gratuitamente per gli iscritti al congresso.

Nelle attuali necessità di distanziamento sociale, il congresso si svolgerà tutto in modalità live telematica, con presentazioni, discussioni e tavole rotonde in diretta. Gli interventi verranno comunque registrati e resi disponibili ai partecipanti nelle due settimane successive alla chiusura del congresso, con possibilità di contatto e discussione con i presentatori.

COMITATO SCIENTIFICO

Gaetano Guerra
Angela Agostiano
Gabriele Costantino
Gianluca Farinola
Michael Assfalg
Paolo Caliceti
Valeria D’Auria
Vito Di Noto
Martino Di Serio
Salvatore Failla
Alceo Macchioni
Fulvio Magni
Antonio Marcomini
Giovanni Marletta
Maria Cristina Menziani
Claudio Minero
Gianluca Sbardella
Margherita Venturi

COMITATO ORGANIZZATORE

Elena Selli – Coordinatore
Alessandro Abbotto
Domenico Albanese
Angiolina Comotti
Rinaldo Psaro
Alessandro Sacchetti

DELEGATI DI DIVISIONE

CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI

Ezio Bolzacchini	ezio.bolzacchini@unimib.it
Lucia Toniolo	lucia.toniolo@polimi.it

CHIMICA ANALITICA

Marco Orlandi	marco.orlandi@unimib.it
Patrizia Mussini	patrizia.mussini@unimi.it

CHIMICA FARMACEUTICA

Paola Conti	paola.conti@unimi.it
Giulio Vistoli	giulio.vistoli@unimi.it

CHIMICA FISICA

Elena Selli	elena.selli@unimi.it
Moreno Meneghetti	moreno.meneghetti@unipd.it

CHIMICA INDUSTRIALE

Ilenia Rossetti	ilenia.rossetti@unimi.it
Antonella Salvini	antonella.salvini@unifi.it

CHIMICA INORGANICA

Emma Gallo	emma.gallo@unimi.it
Francesco Ruffo	francesco.ruffo@unina.it

CHIMICA ORGANICA

Alessandro Abbotto	alessandro.abbotto@unimib.it
Andrea Pace	andrea.pace@unipa.it

DELEGATI DI DIVISIONE

CHIMICA DEI SISTEMI BIOLOGICI

Jussara Amato	jussara.amato@unina.it
Danilo Milardi	danilo.milardi@cnr.it

DIDATTICA CHIMICA

Ugo Cosentino	ugo.cosentino@unimib.it
Sergio Palazzi	studio@kemia.it

ELETTROCHIMICA

Luigi Falciola	luigi.falciola@unimi.it
Riccardo Ruffo	riccardo.ruffo@unimib.it

SPETTROMETRIA DI MASSA

Giuseppe Paglia	beppepaglia@gmail.com
Matteo Audano	matteo.audano@unimi.it

CHIMICA TEORICA E COMPUTAZIONALE

Michele Ceotto	michele.ceotto@unimi.it
Claudio Greco	claudio.greco@unimib.it

CHIMICA PER LE TECNOLOGIE

Alessandro Sacchetti	alessandro.sacchetti@polimi.it
Fabio Ganazzoli	fabio.ganazzoli@polimi.it

TECNOLOGIA FARMACEUTICA

Nunzio Denora	nunzio.denora@uniba.it
Rosario Pignatello	rosario.pignatello@unict.it

XXVII Congresso Nazionale della Società Chimica Italiana
“SCI 2021”, 14-23 settembre 2021

	14 settembre	15 settembre	16 settembre	17 settembre
09:30-10:30		**Lavori Divisioni** **14 Sessioni Parallele** 1 (ABC) + 2 (FAR) + 2 (FIS) + 3 (INO) + 2 (TEC) + 3 (ELE) + 1 (TFA)	**Lavori Divisioni** **14 Sessioni Parallele** 3 (ANA) + 3 (FIS) + 2 (IND) + 3 (ORG) + 1 (CSB) + 1 (ELE) + 1 (TEC)	**Lavori Divisioni** **14 Sessioni Parallele** 2 (ABC) + 2 (FAR) + 2 (FIS) + 3 (INO) + 1 (TEC) + 3 (ELE) + 1 (TFA)
10:30-11:00				
11:00-11:30				
11:30-12:00				
12:00-12:30			**Break**	
12:30-13:00			**ASSEMBLEE DIVISIONALI** **14 sessioni parallele** **(12:30 - 14:45)**	
13:00-14:00		**Break**		**Break**
14:00-14:30		ePoster Session		ePoster Session
14:30-15:00				
15:00-16:00	**APERTURA DEL CONGRESSO** *Saluti* **Maria Cristina MESSA** Ministro del MUR **Maria Chiara CARROZZA** Presidente CNR **Plenary Lecture del Prof. Stanley WHITTINGHAM** **PREMIO NOBEL PER LA CHIMICA 2019** Binghamton University, State University of New York, USA	**Lavori Divisioni** **14 Sessioni Parallele** 3 (ANA) + 2 (FAR) + 1 (IND) + 4 (ORG) + 1 (CSB) + 1 (DID) + 1 (MAS) + 1 (TEO)	Sessione plenaria 2 ***La Chimica per il Benessere e la Qualità della Vita*** **Gunda I. GEORG** University of Minnesota, Department of Medicinal Chemistry, USA	**Lavori Divisioni** **14 Sessioni Parallele** 3 (ANA) + 1 (IND) + 1 (ABC) + 4 (ORG) + 1 (CSB) + 1 (DID) + 1 (MAS) + 2 (TEO)
16:00-16:30	Sessione plenaria 1 ***Chimica, la Scienza al Centro*** **PREMIAZIONE DELLE MEDAGLIE SCI 2020**		**Juliane HOLLENDER** Swiss Federal Institute of Aquatic Science and Technology	
16:30-17:00			**Luis Liz MARZAN** CIC biomaGUNE, San Sebastián, Spain	
17:00-:17:30	Break		**Patrick COUVREUR** Université Paris-Sud France	
17:30-18:00	***Elsevier’s Lecture*** **Ralf METZLER** Theoretical Physics, University of Potsdam, Germany		**Mark NOE** vice-Presidente della Pfizer	
18:00-18:30	Live Q&A Sessione 1	Discussione	Live Q&A Sessione 2	Discussione
18,30-19,30	ePoster	e-poster	e-poster	e-poster

	20 settembre	21 settembre	22 settembre	23 settembre
09:30-10:30	**Lavori Divisioni** **3 Sessioni Parallele** 3 (ORG)	**Lavori Divisioni** **14 Sessioni Parallele** 2 (ABC) + 2 (FAR) + 2 (FIS) + 3 (INO) + 1 (TEC) + 3 (ELE) + 1 (TFA)	Gruppo Giovani **Yan LIANG** University of Science and Technology of China	**Lavori Divisioni** **13 Sessioni Parallele** 3 (ANA) + 3 (FIS) + 1 (IND) + 3 (INO) + 3 (ORG)
10:30:11:00			**2 Sessioni Parallele**	
11:00-11:30				
11:30-12:30				
12:30-13:00	**Break**			

13:00-14:00	**ASSEMBLEA GENERALE** **(13:00 - 14:45)**	Break	Break	Break
14:00-15:00		ePoster Session	ePoster Session	ePoster Session
15:00-16:00	Sessione plenaria 3 ***La Chimica per la Cultura*** **Prof. Roald HOFFMANN** **PREMIO NOBEL PER LA CHIMICA 1981** Department of Chemistry Cornell University Ithaca USA	**Lavori Divisioni** **12 Sessioni Parallele** 3 (ANA) + 1 (IND) + 4 (ORG) + 1 (CSB) + 1 (DID) + 1 (MAS) + 1 (TEO)	**Eventi Satellite** **5 Sessioni Parallele** **- Principi attivi e formulazioni in ambito cosmetico** **- Ruolo della Chimica nella produzione e controllo dei farmaci biotecnologici** **- Valorizzazione di scarti di filiere produttive** **- Sostenibilità di polimeri e compositi** **- La conversione e lo stoccaggio dell'energia chimica in energia elettrica, nella vita odierna e nella società futura**	Sessione plenaria 4 ***La Chimica per l'Industria del Futuro*** **Luigi NICOLAIS** Research Policy Advisor to MUR **Avelino CORMA** Institute of Chemical Technology Polytechnical University of Valencia, Spain
16:00-16:30	**Maria Perla COLOMBINI** Dipartimento di Chimica e Chimica Industriale, Università di Pisa			**Lidia ARMELAO** Direttore del Dipartimento di Scienze Chimiche e Tecnologia dei Materiali, CNR
16:30-17:00	Break			Break
17:00-18.00	TAVOLA ROTONDA **Divulgazione scientifica e immagine della Chimica** Partecipano: **Piero Angela** **Silvano Fuso** **Massimo Polidoro** **Luigi Campanella** Coordina: **Giorgio Cevasco**			**Nausicaa ORLANDI** Presidente Federazione Nazionale Ordini Chimici e Fisici **Mario MARCHIONNA** Corporate Head Technology Innovation Saipem
18:00-18:30	Live Q&A Sessione 3	Discussione	Live Q&A	Live Q&A Sessione 4
18:30-19:30	ePoster	e-poster	e-poster	**CONCLUSIONI E CHIUSURA DEL CONGRESSO**

Programma dei LAVORI di DIVISIONE - 15 settembre mattina

Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

ABC 01

09.30-09.35		**Antonio Marcomini**	*Opening*
09.35-10.00	**ABC IL001**	**Demetrios Anglos**	*Exploring heritage materials and objects via laser spectroscopies*
10.00-10.15	**ABC OR001**	**Gianluigi de Gennaro**	*Sars-CoV-2 airborne transmission: indoor and outdoor implications*
10.15-10.30	**ABC OR002**	**Eleonora Balliana**	*Silk and sanitizing solutions: the need to protect visitor and artworks*
10.30-10.45	**ABC OR003**	**Luca Ciacci**	*Combining the highest degradation efficiency with the lowest environmental impact in zinc oxide based photocatalytic systems*
10.45-11.00	**ABC OR004**	**Cecilia Velino**	*PROCRAFT project: conservation strategies of aircraft heritage from excavation to museum*
11.00-11.30	**break**		
11.30-11.45	**ABC OR005**	**Luca Ferrero**	*Airborne microplastics over the Baltic: influence of sea emissions*
11.45-12.00	**ABC OR006**	**Alessandra Bigogno**	*An indoor air pollution evaluation of the Quarto Stato museum*
12.00-12.15	**ABC OR007**	**Elena Badetti**	*Grafting on metal oxide nanoparticles surface reduces the toxicity of catechols*
12.15-12.30	**ABC OR008**	**Alessandro Ciccola**	*The new shades of the XX century: investigation of ACNA dyes through Raman spectroscopy and HPLC-MS*
12.30-12.45	**ABC OR009**	**Angelo Fenti**	*In Situ Electrochemical Oxidation for Destructive Treatment of PFAS*
12.45-13.00	**ABC OR010**	**Sabina Licen**	*Data fusion techniques based on Self-Organizing Map algorithm for the integration of different source/frequency instrumental data and ancillary information for environmental impact assessment*

Divisione CHIMICA FARMACEUTICA (FAR)

FAR 01

09.30 - 10.00	**FAR KN001**	**Giuseppe Campiani**	*Old but Gold: tracking the new guise of histone deacetylases as biomarkers and therapeutic targets in rare diseases. The role of isoform 6*
10.00 - 10.30	**FAR KN002**	**György M. Keserű**	*The role of the secondary binding pocket in GPCR pharmacology*
10.30 - 10.45	**FAR OR001**	**Agnese Pippione**	*Targeting prostate cancer with multiple-targeting ligands: activity on both AKR1C3 enzyme and androgen receptor*

15 settembre - mattina

10.45 - 11.00	**FAR OR002**	**Andrea Spinaci**	*Synthesis and characterization of new A3 adenosine receptors ligands as potential anti-cancer agents*
11.00 - 11.15	**break**		
11.15 - 11.45	**FAR KN003**	**Tracey Pirali**	*The power of multi-component reactions in drug discovery: soft drugs, PROTACs and more*
11.45 - 12.00	**FAR OR005**	**Simona Musella**	*Identification and characterization of a potent TRPM8 antagonists with in vivo analgesic properties*
12.00 -12.15	**FAR OR006**	**Letizia Crocetti**	*Synthesis of pyrazolo[1,5-a]quinazolines as ligand of α1β3γ2-GABAA receptor subtype and molecular modelling studies*
12.15 -12.30	**FAR OR007**	**Carmine Ostacolo**	*Discovery of CP86, a potent neuronal Kv7 channel activator with in vivo anticonvulsant effects*
12.30 - 13.00	**FAR KN004**	**Marco Radi**	*Navigating the antiviral drug discovery space: exploring different routes toward new broad-spectrum agents*

FAR 02

10.30 - 10.45	**FAR OR003**	**Francesca Musumeci**	*Design, synthesis, and biological evaluation of a new series of pyrazolo[3,4-d]pyrimidines active as SGK1 inhibitors. A lead optimization study*
10.45 - 11.00	**FAR OR004**	**Giuseppe La Regina**	*New pyrroles derivatives as anti-glioblastoma and anti-chronic myeloid leukemia agents*
11.00 - 11.45	**break**		
11.45 - 12.00	**FAR OR008**	**Laura Scalvini**	*N-Acylethanolamine acid amidase (NAAA): mechanism of palmitoylethanolamide hydrolysis revealed by mechanistic simulations*
12.00 -12.15	**FAR OR009**	**Leonardo Brunetti**	*Multiple causes, multiple targets: FAAH as a centerpiece for therapy of multifactorial pathologies*
12.15 -12.30	**FAR OR010**	**Rita Turnaturi**	*Influence of the N-substituent of (−)-cis-N-Normetazocine in the modulation of the functional profile at MOR, DOR and KOR: from agonist to antagonist through multitarget ligands*

15 settembre - mattina

Divisione CHIMICA FISICA (FIS)

FIS 01

Physical chemistry for Nanomaterials I

09:30-10:00	**FIS KN001**	**Marco Laurati**	*Blunt-end driven assembly of star-like dsDNA coated colloids*
10:00-10:15	**FIS OR001**	**Carlo Nazzareno Dibenedetto**	*Fabrication and spectroscopic investigation of Quantum Dots dimers*
10:15-10.30	**FIS OR002**	**Giovanni LiDestri**	*Forces between nanoparticels at the air/water interface: the role of the ligand chain length*
10:30-10.45	**FIS OR003**	**Davide Peddis**	*Interplay between inter- and intraparticle interactions in bi-magnetic core/shell nanoparticles*
10:45-11:00	**FIS OR004**	**Maryam Abdolrahimi**	*XAS Study of Molecular Coated Manganese Zinc Ferrite Nanoparticles*
11:00-11.15	**FIS OR005**	**Sawssen Slimani**	*Hybrid Spinel Iron Oxide Nanoarchitecture Combining Crystalline and Amorphous Parent Material*
11:15-11.30	**FIS OR006**	**Marco Fabbiani**	*Porous materials for hybrid functional nanocomposites: metal and organic nanowires confined in zeolites and mesoporous silica*
11.30-11.45	**break**		

Physical chemistry for Nanomaterials II

11:45-12:00	**FIS OR007**	**Grazia ML Messina**	*Surfactant vesicles and polysaccharides interactions with cellulose nanocrystals*
12:00_12:15	**FIS OR008**	**Simona Ricci**	*Highly efficient green inkjet printed nanostructured electrodes and SERS substrates*
12:15-12.30	**FIS OR009**	**Marcello Condorelli**	*Ag nanoflowers as single particle SERS active platform*
12:30-12:45	**FIS OR010**	**Valentina Mameli**	*57Fe Mössbauer Spectroscopy and DC magnetometry for the identification of Fe-bearing ultrasmall nanophases in inorganic ordered porous matrixes*
12:45-13:00	**FIS OR011**	**Giovanni Ferraro**	*Controlled decoration of plastic surfaces with metal nanostructures*
13:00-13:15	**FIS OR012**	**Roberta Ruffino**	*“Distorted” self-assembly of polymer thin films at nano-curved surfaces*

FIS 02

PhysicalChemistry for Biomedical Applications I

09:30-10:00	**FIS KN002**	**Paola Sassi**	*Spectroscopic markers of heart failure: a Raman and FTIR study*
10:00-10:15	**FIS OR013**	**Nunzio Tuccitto**	*Quantum Dots Enable Digital Communication Through Biological Fluids*

10:15-10.30	**FIS OR014**	**Elisabetta Fanizza**	*Plasmonic mesoporous silica coated copper sulfide nanoparticles as Near Infrared absorbing photothermal agents*
10:30-10.45	**FIS OR015**	**Rossella Labarile**	*Coating photosynthetic Rhodobacter sphaeroides with polydopamine*
10:45-11:00	**FIS OR016**	**Marco Fornasier (Vincitore del Premio Semerano)**	*A polyphosphoester analog of Pluronic F127 enhances the biocompatibility of monoolein-based cubosomes*
11:00-11.15	**FIS OR017**	**Alberta Terzi**	*X-ray Scattering Scanning Microscopies – novel diagnostic tools of pathologic tissues. A focus on aneurysms, breast cancer and diabetes*
11:15-11.30	**FIS OR018**	**Federica D'Aria**	*G-quadruplex within KRAS gene promoter: a physicochemical study*
11.30-11.45	**break**		

PhysicalChemistry for Biomedical Applications II

11:45-12:00	**FIS OR019**	**Vincenzo De Leo**	*Liposome/Polymer Assembly for Oral Delivery of Curcumin*
12:00_12:15	**FIS OR020**	**Monica Mura**	*Nanoantibiotics: design of multifunctional MSN nanosystems containing both antibiotic and copper ions to combat bone infection*
12:15-12.30	**FIS OR023**	**Elena Piacenza**	*Innovative and green synthesis of biocompatible Selenium nanoparticles in a confined environment with promising antimicrobial activity*
12:30-12:45	**FIS OR024**	**Jennifer Gubitosa**	*Green synthesis of Gold nanoparticles by using grape seeds wastewater: physico-chemical characterization and investigation of their related antioxidant features for cosmetic and biomedical applications*

Divisione CHIMICA INORGANICA (INO)

INO 01

9.30 - 10.30	**INO PZ001**	**Frank Neese**	*Deciphering Inorganic Chemistry Riddles Through a Combination of Spectroscopy and Quantum Chemistry*
10.30 - 10.45	**INO OR001**	**Roberto Gobetto**	*Innovative Mn and Re catalysts for CO2 Photo- and Electro-Reduction*
10.45 - 11.00	**INO OR002**	**Ilaria Barlocco**	*Disclosing the role of Gold on Palladium - Gold alloyed catalysts in formic acid decomposition*
11.00 - 11.15	**INO OR003**	**Cristina Pavan**	*Nearly free silanols on silica surface: a new paradigm for particle toxicology*
11.15-11.30	**break**		

15 settembre - mattina

11.30 - 11.45	**INO OR004**	**Massimo Christian D'Alterio**	*A combined theoretical and experimental investigation of a new class of [N,O-] imidazo[1,5-a]pyrid-3-yl)phenolate Zn(II) catalysts for the ring opening polymerization of lactide*
11.45 - 12.00	**INO OR005**	**Linda Leone**	*Highly selective indole oxidation promoted by a Mn-containing mini-enzyme*
12.00 - 12.15	**INO OR006**	**Javier Martí-Rujas**	*Synthesis and structural properties of isostructural Zn(II) M12L8 poly-[n]-catenane using the 2,4,6-tris(4-pyridyl)benzene (TPB) ligand*
12.15 - 12.30	**INO OR007**	**Francesco Fagnani**	*Three novel families of cyclometalated platinum(II) complexes with remarkable luminescence properties*
12.30 - 13.00	**INO IL001**	**Viktoria Gessner**	*Metallated Ylides: Powerful Reagents for the Stabilization of Reactive Main Group Species and Ligands in Catalysis*

INO 02

10.30 - 10.45	**INO OR008**	**Michele Benedetti**	*“NMR effective molecular radius” of coordinated ammonia*
10.45 - 11.00	**INO OR009**	**Chiara Salvitti**	*Redox reactivity of transition metal dioxide anions towards sulfur dioxide in the gas phase*
11.00 - 11.15	**INO OR010**	**Silvia Ruggieri**	*New chiral heteroleptic Eu(III)/Tb(III)/Yb(III)-based luminescent complexes designed for different applications*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR011**	**Tiziano Marzo**	*Oxaliplatin binds angiogenin and exerts high antiangiogenic effects in PC-3 cancer cells at non-cytotoxic concentration*
11.45 - 12.00	**INO OR012**	**Luca Spitaleri**	*Covalently conjugated gold–porphyrin nanostructures*
12.00 - 12.15	**INO OR013**	**Nicola Panza**	*Ferrate salts as stand-alone catalysts for chemical fixation of CO2 into epoxides and aziridines*
12.15 - 12.30	**INO OR014**	**Elena Lucenti**	*Cyclic triimidazole: an appealing and versatile ligand for the preparation of emissive d9 and d10 metal derivatives*

INO 03

10.30 - 10.45	**INO OR015 premio Wiley**	**Thomas Scattolin**	*Palladium organometallic complexes as promising anticancer agents*
10.45 - 11.00	**INO OR016**	**Caterina Damiano**	*Efficient and low-cost metal-free Porphyrin/TBACl system for the CO2 valorization into N alkyl and N aryl oxazolidin-2-ones*
11.00 - 11.15	**INO OR017**	**Carlo Nervi**	*Transition metal complexes as redox catalysts for CO2 conversion*
11.15-11.30	**break**		

11.30 - 11.45	**INO OR018**	**Cristina Tubaro**	*Gold(I) and gold(III) complexes with thioether- and phosphonium- functionalized N-heterocyclic carbene ligands*
11.45 - 12.00	**INO OR019**	**Marco Baron**	*Manganese(III) complexes with tetradentate O^C^C^O ligands: synthesis, characterization and preliminary catalytic studies on the CO2 cycloaddition with epoxides*
12.00 - 12.15	**INO OR020**	**Roberto Esposito**	*MOF catalyzed ketalization of glycerol into solketal*
12.15 - 12.30	**INO OR021**	**Francesco Ferretti**	*Heterocycles from nitro compounds: CO surrogates in the Pd catalyzed synthesis of carbazoles*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)

TEC 01

09.30 - 10.00	**TEC IL001**	**Alberto Rainer**	*Nanogels as smart drug delivery systems*
10.00 - 10.15	**TEC KN001**	**Claudia Espro**	*Hydrothermal Carbonization as a sustainable approach for the single-step upgrading of industrial citrus processing waste into platform chemicals and biocarbon*
10.15 - 10.30	**TEC KN002**	**Fabrizio Monica**	*Chemistry of materials for energy technologies*
10.30 - 10.40	**TEC OR001**	**Virginia Venezia**	*Biowaste as valuable resource: humic acids valorization into multifunctional materials*
10.40 - 10.50	**TEC OR002**	**Francesco Mauriello**	*Sustainable Valorization of Anchovy Leftovers into Value Added Chemicals, Products and Energy*
10.50 - 11.00	**TEC OR003**	**Carlo Punta**	*Eco-design of Cellulose NanoSponges for water decontamination*
11.00 - 11.10	**TEC OR004**	**Ermelinda Bloise**	*CNSL components as green building-blocks for bio-based nanovesicles*
11.10 - 11.30	**Discussion**		
11.30 - 11.50	**Break**		
11.50 - 12.00	**TEC OR005**	**Manfredi Caruso**	*N-Hydroxyphthalimide role in Aerobic Oxidations: Homogeneous versus Heterogeneous Catalysis*
12.00 - 12.10	**TEC OR006**	**Laura Riva**	*Co-Polymeric Nanosponges from Cellulose Biomass as Heterogeneous Catalysts for Organic Reactions*
12.10 - 12.20	**TEC OR007**	**Serena Regina**	*Use of a bio-derived polymer as crosslinking agent for stable-polyvinyl alcohol membrane development*
12.20 - 12.30	**TEC OR008**	**Simona Sabbatini**	*Thermal-Oxidative Stability of PHBV/LDH Nanocomposites*
12.30 - 12.50	**Discussion**		

12.50 - 13.00	**TEC OR009**	**Angela Marotta**	*Furan as platform molecule in the production of greener epoxy-resins*
13.00 - 13.10	**TEC OR010**	**Franca Castiglione**	*Insights on Ionic Liquids structure and dynamics: NMR methods and recent advances*
13.10 - 13.20	**TEC OR011**	**Giselle de Araujo Lima e Souza**	*Ionic conductivity and thermal characterization of DBU-based protic ionic liquids*
13.20 - 13.30	**TEC OR012**	**Maria Enrica Di Pietro**	*Deep Eutectics: what is inside the solvents for the 21st century?*
13.30 - 13.50	**Discussion**		

TEC 02

10.30 - 10.40	**TEC OR013**	**Giulio Pota**	*Mesoporous Silica Nanoparticles: a powerful platform for biocatalysis*
10.40 - 10.50	**TEC OR014**	**Antonella Satira**	*Tandem Catalytic Upgrading of Limonene and Methyl Levulinate promoted by Pd-based Catalysts*
10.50 - 11.00	**TEC OR015**	**Francesco Parrino**	*Synthesis, characterization, and photocatalytic activity of Eu doped ZnO prepared by supercritical antisolvent precipitation route*
11.00 - 11.10	**TEC OR016**	**Cristina Leonelli**	*Microwave-assisted synthesis and isopropanol extraction in the preparation of TiO2 nanoparticle suspensions*
11.10 - 11.30	**Discussion**		
11.30 - 11.50	**Break**		
11.50 - 12.00	**TEC OR017**	**Aurelio Bifulco**	*Hybrid Strategies for the Improvement of the Flame Retardancy of in-situ Silica-Epoxy Nanocomposites cured with Aliphatic Hardener*
12.00 - 12.10	**TEC OR018**	**Isabella Lancellotti**	*Chemical stabilization in a single step process: geopolymerization of tannery wastewater pollutants*
12.10 - 12.20	**TEC OR019**	**Ambra M. Fiore**	*Hematite nanoparticles as promising catalyst*
12.20 - 12.50	**Discussion**		
12.50 - 13.00	**TEC OR021**	**Vincenzina Barbera**	*Functionalization of graphene related materials with biosourced C-3 and C-6 building blocks. From synthesis to applications*
13.00 - 13.10	**TEC OR022**	**Sabina Alessi**	*Polymer/rubber nanofibrous interleaves for the enhancement of delamination resistance of CFRP laminates*
13.10 - 13.20	**TEC OR023**	**Laura Tripaldi**	*Silica Hairy Nanoparticles in Rubber Nanocomposites*
13.20 - 13.30	**TEC OR024**	**Mariachiara Miceli**	*Titanosilicalite as Nickel Support for Methanation Reaction*
13.30 - 13.50	**Discussion**		

Divisione ELETTROCHIMICA (ELE)

ELE 01

09.30 - 10.00	**ELE_KN01**	**Patrizia Mussini**	*Enantioselective Voltammetry & Chiroptical Spectroscopy: Exploring Intriguing Analogies and Connections*
10.00 - 10.15	**ELE_OR02**	**Elisabetta Petri**	*Electrochemically responsive soft actuators*
10.15 - 10.30	**ELE_OR03**	**Carmelo Lo Vecchio**	*NiFe oxide co-catalyst for an enhanced water splitting in photo-electrochemical cells*
10.30 - 10.45	**ELE_OR04**	**Marco Piccinni**	*Synthesis and water dispersion of nickel-iron layered double hydroxides for energy storage applications*
10.45 - 11.00	**ELE_OR05**	**Daniele Rocco**	*Anodic Dimerization of New Donor-Acceptor Oligothiophenes: Electrochemical and Solvatochromic Behavior*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE_KN06**	**Peter Fischer**	
11.45 - 12.00	**ELE_OR07**	**Giovanni Crivellaro**	*A complex electrochemistry triggering the operation of Vanadium Redox Flow Batteries*
12.00 - 12.15	**ELE_OR08**	**Giampaolo Lacarbonara**	*A spectroelectrochemical study of copper chloro-complexes for high performance copper redox flow batteries*
12.15 - 12.30	**ELE_OR09**	**Jorge Montero**	*Ferrocene and viologen derivatives as electrolytes for pH neutral aqueous organic redox flow batteries*

ELE 02

09.30 - 10.00	**ELE KN10**	**Giovanni Valenti**	*New Insights Into Electrogenerated Chemiluminescence Mechanism for the Enhancement of Bioanalytical Performance*
10.00 - 10.15	**ELE OR11**	**Sara Bonacchi**	*SpectroElectrochemistry of Metal Nanoclusters:new insights into the origin of the photoluminescence*
10.15 - 10.30	**ELE OR12**	**Marco Mazzucato**	*How Decisive is the Iron Precursor Ligand in Fe-N-C Single-Site Formation and Activity for Oxygen Reduction Reaction?*
10.30 - 10.45	**ELE OR13**	**Mattia Parnigotto**	*Water Loss Predictive Tests in Flooded Lead-Acid Batteries*
10.45 - 11.00	**ELE OR14**	**Mattia Reato**	*Electron Transfers in Films of Atomically Precise Metal Nanoclusters*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE KN15**	**Alessandro Minguzzi**	*In situ/operando X-ray absorption spectroscopy: a swiss-knife for studying (photo)electrodes*

11.45 - 12.00	**ELE OR16**	**Francesco De Bon**	*Para substituted pyridines ligands forms highly active catalysts for ATRP*
12.00 - 12.15	**ELE OR17**	**Danilo Dini**	*EQCM analysis of the process of electrochemical insertion in regioregular alkyl-susbtituted polyterthiophene during n-doping*
12.15 - 12.30	**ELE OR18**	**Matteo Grattieri**	*Bio-inspired intact bacteria-based biohybrid photoanodes*

ELE 03

09.30 - 10.00	**ELEKN19**	**Marc Koper**	*Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide*
10.00 - 10.15	**ELEOR20**	**Maruccia Elisa**	*Nitrogen-containing ordered mesoporous carbons applied as CO2 adsorbents and anode materials in energy storage devices*
10.15 - 10.30	**ELEOR21**	**Fortunati Alessia**	*Ionic liquids for capture and electrochemical Conversion of CO2*
10.30 - 10.45	**ELEOR22**	**Moro Miriam**	*Carbon Nanostructures decorated with Cerium Oxide as selective electrocatalysts for CO2 reduction*
10.45 - 11.00	**ELEOR23**	**Guzman Hilmar**	*CuZnAl-based oxide catalysts for the electrochemical CO2 conversion*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELEKN24**	**Monica Santamaria**	*Electrochemical surface treatments to improve corrosion resistance of light alloys*
11.45 - 12.00	**ELEOR25**	**Zoli Maddalena**	*Facile and scalable synthesis of Cu2O-SnO2 catalyst for the photoelectrochemical CO2 conversion*
12.00 - 12.15	**ELEOR26**	**Magni Mirko**	*Cathodic Plasma Electrolysis & Recovery of Zinc as Coating*
12.15 - 12.30	**ELEOR27**	**Poli Federico**	*Sustainable strategies to improve MFC power output by green supercapacitors and supercapacitive components*

Divisione TECNOLOGIA FARMACEUTICA (TFA)

TFA 01

09.30 - 10.00	**TFA IL001**	**Elias Fattal**	*Lipid and dendrimer-based nanomedicines for siRNA*
10.00 - 10.30	**TFA IL002**	**Stefano Colloca**	*Set up of large scale production process for GRAd-COV2 vaccine*
10.30 - 10.45	***Discussion***		
10.45 - 11.00	**break**		

15 settembre - mattina

11.00 - 11.15	**TFA OR001**	**Ilaria Arduino**	*Microfluidic preparation and characterization of iRGD-functionalized solid lipid nanoparticles for targeted delivery*
11.15 - 11.30	**TFA OR002**	**Angela Bonaccorso**	*Response Surface Methodology for the optimization of Nanogels Polyelectrolyte Complex intended for Ovalbumin nasal delivery*
11.30 - 11.45	**TFA OR003**	**Ilaria Filippin**	*Cellulase as active excipient in HPMC prolonged-release matrices: a novel approach to zero-order kinetics*
11.45 - 12.00	**TFA OR004**	**Stefania Petralito**	*Remote magneto-mechanical actuation of magnetoliposomes by alternating or pulsed magnetic fields*
12.00 - 12.15	**TFA OR005**	**Emma Piacentini**	*Controlled and tunable polymeric micro/nano particles production using membrane technology*
12.15 - 12.30	**TFA OR006**	**Giovanna Rassu**	*Crocetin as both neuroprotective agent and cross-linker for sericin for obtaining new nasal bioactive nanoparticles*
12.30 - 12.45	**TFA OR007**	**Federica Rinaldi**	*Rifampicin loaded liposomes for Mycobacterium abscessus infection treatement: intracellular uptake and antibacterial activity evaluation*
12.45 - 13.00	**TFA OR008**	**Mattia Tiboni**	*An affordable approach to scalable nanomedicine manufacturing: 3D printed microfluidics*
13.00 - 13.15	**TFA OR009**	**Siyuan Deng**	*Development and Characterization of a Novel Redox-responsive Core-shell Structure Nanohydrogel as Intracellular Delivery System*
13.15-13.30	***Discussion***		

Programma dei LAVORI di DIVISIONE - 15 settembre pomeriggio

Divisione CHIMICA ANALITICA (ANA)

ANA 01

15.00 - 15.10	**ANA PL001**	**Claudio Minero**	*INTRODUZIONE*
15.10 - 15.30	**ANA PZ001**	**Luigia Sabbatini**	*Contaminarsi fa bene alla ricerca*
15.30 - 15.50	**ANA PZ002**	**Luigi Mondello**	*Recent Developments in Mass spectrometry and Cutting Edge Scientific Innovation to Characterize Complex Samples*
15.50 - 16.10	**ANA IL001**	**Susy Piovesana**	*New trends for the enrichment and liquid chromatography-mass spectrometry analysis of peptides with protein post-translational modifications*
16.10 - 16.30	**ANA KN001**	**Flavio A. Franchina**	*The value of multidimensional chromatography coupled to mass spectrometry for the non-targeted metabolite profiling of natural products*
16.30 - 16.45	**ANA OR001**	**Alessia Arena**	*Mineral oil investigation in omega-3 rich lipid supplements by using multidimensional liquid-gas chromatography*
16.45 - 17.00	**ANA OR002**	**Carmela Maria Montone**	*Untargeted characterization and quantitative analysis of underivatized fatty acids in Chlorella vulgaris microalgae*
17.00 - 17.15	**ANA OR003**	**Lorenzo Cucinotta**	*Simultaneous Enantiomeric and Isotopic Ratio evaluation of target terpenes in Cannabis sativa essential oils through Enantio-MDGC-C-IRMS*
17.15 - 17.30	**ANA OR004**	**Gemma De Grazia**	*Evaluation of cryogenic effect for target VOCs isolation by a preparative multidimensional gas chromatographic system*
17.30 - 17.45	**ANA OR005**	**Rosangela Elliani**	*DEVELOPMENT OF A RAPID AND SIMPLE PROTOCOL FOR THE ASSAY OF PARABENS AND BISPHENOLS IN HUMAN SALIVA BY SOLID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-TRIPLE QUADRUPOLE MASS SPECTROMETRY*
17.45 - 18.00	**ANA OR006**	**Antonio Ferracane**	*Simultaneous determination of 88 multi-class pesticide residues in four vegetable matrices using reduced QuEChERS extraction and flow-modulated comprehensive two-dimensional gas chromatography-triple quadrupole mass spectrometry*
18.00 - 18.15	**ANA OR007**	**Micaela Galletta**	*Evaluation of use of hydrogen as carrier gas in flow-modulation comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry*

18.15 - 18.30	**ANA OR008**	**Anna Illiano**	*LC-MRM/MS assay for the quantification of some hormonal proteins in serum and follicular fluid of women undergoing in vitro fertilization*

ANA 02

15.50 - 16.10	**ANA KN002**	**Clemente Bretti**	*Removal of environmentally relevant cations: polymer inclusion membranes (PIMs)*
16.10 - 16.30	**ANA KN003**	**Francesco Pellegrino**	*A New Strategy for Overcoming the Volcano in Water Photosplitting: Controlled Periodic Illumination*
16.30 - 16.45	**ANA OR009**	**Raghav Dogra**	*Preliminary evaluation of Magnetic Nanoparticles for glyphosate contaminated water remediation*
16.45 - 17.00	**ANA OR010**	**Federico Girolametti**	*Evaluation of mercury content in red mullet (Mullus barbatus) muscle from the Adriatic Sea in relation to biological factors and sampling area: risk assessment for human consumption*
17.00 - 17.15	**ANA OR011**	**Marco Minella**	*Experimental evaluation of Fenton oxidation coupled with membrane distillation for produced water treatment: benefits, challenges and effluent toxicity*
17.15 - 17.30	**ANA OR012**	**Donatella Nardiello**	*Nanoconfined liquid phase nanoextraction: an innovative extraction technique for ex-situ and in-situ rapid and quantitative determination of benzene derivatives in seawater*
17.30 - 17.45	**ANA OR013**	**Gabriella Pinto**	*Characterization of polyphenolic compounds in food and industrial wastes*
17.45 - 18.00	**ANA OR014**	**Luca Rivoira**	*Iterative protocols for the extraction and quantitation of microplastics from marine sediments and oysters*
18.00 - 18.15	**ANA OR015**	**Saul Santini**	*Validation of a new method for the simultaneous determination of different classes of PBT chemicals in biota samples*
18.15 - 18.30	**ANA OR016**	**Davide Vivado**	*Study of iron speciation in coastal seawater samples of the Ross Sea (Antarctica) by CLE-AdSV*

ANA 03

15.50 - 16.10	**ANA IL002**	**Erika Scavetta**	*Organic Electrochemical Transistors as low cost chemical sensors*
16.10 - 16.30	**ANA IL003**	**Chiara Zanardi**	*Graphene-based electrodes for the detection of biomarkers in sweat*
16.30 - 16.45	**ANA OR017**	**Andrea Bonini**	*A Label-free impedance biosensing assay based on CRISPR/Cas12a collateral activity for bacterial DNA detection*

15 settembre - pomeriggio

16.45 - 17.00	**ANA OR018**	**Tiziano Di Giulio**	*Molecularly imprinted polymers-based impedimetric sensor for metal-ion mediated recognition of a dipeptide*
17.00 - 17.15	**ANA OR019**	**Laura Fabiani**	*Magnetic beads combined with carbon black-based screen-printed electrodes for COVID-19: A reliable and miniaturized electrochemical immunosensor for SARS-CoV-2 detection in saliva*
17.15 - 17.30	**ANA OR020**	**Eleonora Macchia**	*Selective Single-Molecule Detection of clinically relevant biomarkers with an Organic Transistor*
17.30 - 17.45	**ANA OR021**	**Federica Mariani**	*Healthcare monitoring using wearable pH sensors*
17.45 - 18.00	**ANA OR022**	**Vincenzo Mazzaracchio**	*A TiO2 /KuQuinone modified screen-printed photoelectrochemical sensor for NADH detection*
18.00 - 18.15	**ANA OR023**	**Gheorghe Melinte**	*Enhancement of lysozyme detection process by using a gold clusters-based electrochemical aptasensor*
18.15 - 18.30	**ANA OR024**	**Filippo Silveri**	*Redox-active graphene film integrated into a smart device for pesticide biosensing*

Divisione CHIMICA FARMACEUTICA (FAR)
FAR 03

15.00 - 15.45	**FAR MD001**	**Kenneth A. Jacobson**	*Pratesi Medal Lecture - Design and Therapeutic Potential of Adenosine and P2Y Receptor Ligands*
15.45 - 16.00	**FAR PZ001**	**Ciro Milite**	*Modulators of Coactivator-Associated Arginine Methyltransferase 1 (CARM-1): There and Back Again*
16.00 - 16.15	**FAR PZ002**	**Mariateresa Giustiniano**	*Isocyanide Chemistry from the Ground (state) to the Star(s): what’s the point for a medicinal chemist?*
16.15 - 17.00	**FAR MD002**	**Antonello Mai**	*Giacomello Medal Lecture - Lecture for the receipt of the “Giordano Giacomello” medal by the Medicinal Chemistry Division of the Italian Chemical Society*
17.00 - 17.15	**break**		
17.15 - 17.30	**FAR OR011**	**Marilia Barreca**	*Inhibition of non-Hodgkin lymphoma cell growth by pyrrolo[1,2]oxazole derivatives*
17.30 - 17.45	**FAR OR012**	**Laura Braconi**	*A new strategy to overcome multidrug resistance (MDR) in cancer cells: P-gp and hCAXII multitarget inhibitors*
17.45 - 18.00	**FAR OR013**	**Daniela Carbone**	*Synthesis and preclinical evaluation of a new generation of 1,2,4-triazine-based PDK modulators: a novel therapeutic approach to halt cancer growth.*

18.00 -18.15	**FAR OR014**	**Arianna Gelain**	*Unraveling the interaction mechanism of a benzothiadiazole-2,2-dioxide derivative with STAT3: towards novel direct inhibitors*

FAR 04

17.15 - 17.30	**FAR OR015**	**Lucia Tamborini**	*Flow-based redox biotransformations for food and pharma applications*
17.30 - 17.45	**FAR OR016**	**Federica Ianni**	*Stability of chlorogenic acid as model system after household microwave treatment*
17.45 - 18.00	**FAR OR017**	**Ilaria Frosi**	*Comparison of different extraction methods to recover bioactive compounds from corn waste (Zea mays L.)*
18.00 -18.15	**FAR OR018**	**Martina Contente**	*Valorization of food wastes and residues through glycosidases*

Divisione CHIMICA INDUSTRIALE (IND)

IND 01

Sessione congiunta con Gruppo Interdivisionale Catalisi

15.00 - 15.30	**IND KN001 Medaglia Piero Pino**	**Nicoletta Ravasio**	*Catalysis and Green Deal*
15,30 - 15,40	**IND OR001**	**Eleonora Aneggi**	*Solvent free selective oxidation of benzyl alcohol over supported Ru catalysts*
15.40 - 15.50	**IND OR002**	**Denise Cavuoto**	*The role of support wettability and acidity in the hydrogenation of γ-valerolactone over Cu/SiO2 catalyst*
15.50 - 16,00	**IND OR003**	**Tommaso Tabanelli**	*Improved Catalytic Transfer Hydrogenation of alkyl levulinates with alcohols over ZrO2 based catalysts*
16.00 - 16.10	**IND OR004**	**Eleonora Vottero**	*Reconstruction phenomena in a Pt/γ-Al2O3 catalyst under hydrogenation conditions*
16.10 - 16.20	**IND OR005**	**Maila Danielis**	*Structural Evolution and Enhanced Steam Deactivation Resistance of PtPd/CeO2 Methane Oxidation Catalysts Prepared by Dry Milling*
16.20 - 16.30	**IND OR006**	**Gabriella Garbarino**	*Effect of promoters on the performances of Ni-Al2O3 catalysts for CO2 hydrogenation*
16.30 - 16.45	**Discussion**		
16.45 - 17.00	**break**		
17.00 - 17.20	**IND KN002**	**Walter Cabri**	*The Twelve Principles of Green Chemistry Translation Guide for Palladium Catalyzed Cross Coupling Reactions for Active Pharmaceutical Ingredients Sustainable Productions”*
17.20 - 17.30	**IND OR007**	**Roberto Sole**	*The alkoxycarbonylation of protected propargyl alcohols*

17.30 - 17.40	**IND OR008**	**Aleksandr Voronov**	*Unexpected O-5-exo-dig Cyclization of Propargyl Ureas to Oxazoline-2-amines Catalyzed by Silver Salts*
17.40 - 17.50	**IND OR009**	**Francesco Taddeo**	*Kinetics of solketal synthesis promoted by Iron(III) complex*
17.50 - 18.00	**IND OR010**	**Vinayak. Botla**	*Palladium/Norbornene-Catalyzed Synthesis of 2-Iodobiaryls*
18.00 - 18.10	**IND OR011**	**Stefano Econdi**	*Heterogeneous catalysts for the liquid-phase degradation of simulants of organophosphorus chemical warfare agents*
18.10 -18.30	**Discussion**		

Divisione CHIMICA ORGANICA (ORG)

ORG 01

15.00 - 15.30	**Benvenuto e premiazione (sessioni unificate)**		
15:30 - 16:00	**ORG PZ001**	**Anna Bernardi**	***Medaglia Adolfo Quilico*** *At the crossroad between Chemistry and Biology: interfering with the sugar code using glycomimetics*
16.00 - 16.15	**ORG OR001**	**Alessandro Ajo**	*Nanocages and capsules for drug and peptides delivery*
16.15 - 16.30	**ORG OR002**	**Silvana Alfei**	*Cationic Copolymers: A Promising Option in the Treatment of Drug Resistance in Neuroblastoma Cells*
16.30 - 16.45	**ORG OR003**	**Davide Audisio**	*Direct Carbon Isotope Exchange of Pharmaceuticals via Reversible Decyanation*
16.45 - 17.00	**ORG OR004**	**Sara Battista**	*Antibacterial and physicochemical properties of quatsomes formulated with L-prolinol-derived surfactants*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR005**	**Roberta Bernini**	*Hydroxytyrosol, much more than an antioxidant*
17.45 - 18.00	**ORG OR006**	**Andrea Calcaterra**	*Diels-Alder type adducts from Morus nigra as potent inhibitors of Micobacterium tuberculosis PtpB*
18.00 - 18.15	**ORG OR007**	**Fabrizio Chiodo**	*Carbohydrate-Mediated "Innate" Considerations in Designing Vaccine-Candidates*
18.15 - 18.30	**ORG OR008**	**Martina Cirillo**	*Selective Integrin Ligands Promote Cell Internalization of the antineoplastic agent Fluorouracil*

ORG 02

16.00 - 16.15	**ORG OR009**	**Mariapina D'Onofrio**	*Chemoselective disulfide-coupling for the semisynthesis of ubiquitinated forms of the Alzheimer's associated protein tau*

15 settembre - pomeriggio

16.15 - 16.30	**ORG OR010**	**Maria Giulia Davighi**	*New potential carbonic anhydrase inhibitors based on mono and multivalent sugars and iminosugars*
16.30 - 16.45	**ORG OR011**	**Cristina De Castro**	*N-glycan from Paramecium bursaria Chlorella virus MA-1D: reevaluation*
16.45 - 17.00	**ORG OR012**	**Jenny Desantis**	*Design, synthesis, and evaluation of small molecules Proteolysis Targeting Chimeras (PROTACs) to induce androgen receptor degradation*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR013**	**Cristina Di Carluccio**	*Investigation of the molecular recognition of sialoglycans bound to Siglec-like adhesins of Streptococcus gordonii*
17.45 - 18.00	**ORG OR014**	**Rossella Di Guida**	*Structural characterization of the lipooligosaccharide and capsular polysaccharide from the psychrotrophic bacterium Pseudoalteromonas nigrifaciens Sq02*
18.00 - 18.15	**ORG OR015**	**Maria Funicello**	*Switching the anticancer effect to HIV protease inhibition: new heteroaryl-amidic compounds with a pseudo-symmetric core*
18.15 - 18.30	**ORG OR016**	**Dario Gentili**	*Synthesis of small molecules with potential antiviral acitivity against Sars-CoV-2*

ORG 03

16.00 - 16.15	**ORG OR017**	**Vincenzo Algieri**	*Regioselective Synthesis of 1,3,4,5-Tetrasubstituted Pyrazoles by Eliminative Enaminone-Nitrilimine 1,3-Dipolar Cycloaddition*
16.15 - 16.30	**ORG OR018**	**Michael Andresini**	*Nitrogen transfer to sulfenamides: synthesis of sulfinamidines and unexplored sulfinimidate esters as valuable precursors of protected sulfilimines*
16.30 - 16.45	**ORG OR019**	**Marco Ballarotto**	*Substituted 6H-benzo[c]chromenes: synthetic approach via a Diels-Alder/aromatization sequence and computational investigation*
16.45 - 17.00	**ORG OR020**	**Bruno Mattia Bizzarri**	*Aminomaleonitrile inspired prebiotic chemistry as a novel microwave assisted multicomponent tool for the synthesis of imidazole and purine derivatives with anti-influenza activity*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR021**	**Diego Caprioglio**	*The oxidation of phytocannabinoids: a systematic investigation*
17.45 - 18.00	**ORG OR022**	**Marco Colella**	*Use of flow technology for the development of a sustainable synthesis of azetines and azetidines*
18.00 - 18.15	**ORG OR023**	**Dario Corbisiero**	*Enantioselective Synthesis of Polyfunctionalized Isoxazoline Rings: Development of a Methodology for the preparation of Tumor-Oriented Small Molecules*

15 settembre - pomeriggio

18.15 - 18.30	**ORG OR024**	**Massimiliano Cordaro**	*Synthetic Approaches to Molecular Diversity of BODIPY*

ORG 04

16.00 - 16.15	**ORG OR025**	**Vincenzo Mirco Abbinante**	*Highly-fluorinated aromatic diimides for organic electronics:from synthesis to thin-film preparation*
16.15 - 16.30	**ORG OR026**	**Rita Argenziano**	*Functional films from 5,6-dihydroxyindole oligomers and long chain diamines partnership*
16.30 - 16.45	**ORG OR027**	**Giacomo Biagiotti**	*Tailoring the structure of the BODIPY probe in the design of functional fluorescent materials*
16.45 - 17.00	**ORG OR028**	**Davide Blasi**	*Trityl-brominated radicals as building blocks for doublet CPL emitters*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR029**	**Alberto Bossi**	*Porphycenes, a lesser known tetrapyrrolic macrocycle with intriguing properties suitable for in situ sensing*
17.45 - 18.00	**ORG OR030**	**Adriano Parodi**	*Polyhydroxybutyrate as a sustainable platform for the production of chemicals and bio-polymers*
18.00 - 18.15	**ORG OR031**	**Simone Di Noja**	*Transfer of Axial Chirality to the Nanoscale Endows Carbon Dots with Circularly Polarized Luminescence*
18.15 - 18.30	**ORG OR032**	**Claudio Ferdeghini**	*Synthesis and thermal behavior of dicationic ionic liquids*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 01

15.00 - 15.05	**Opening Remarks Presidente Michael Assfalg**		
15.05 - 15.35	**CSB KN001**	**Rommie Amaro**	*Computational Microscopy of SARS-CoV-2*
15.35 - 16.00	**CSB PZ001**	**Luca Mazzei**	*Talking about urease: How the grasp on the molecular aspects of this enzyme can help in counteracting its role in microbiological pathogenesis and environmental issues*
16.00 - 16.15	**CSB OR001**	**Marta De Zotti**	*A pH-Induced Reversible Conformational Switch able to control the Photocurrent Efficiency in a Peptide Supramolecular System*
16.15 - 16.30	**CSB OR002**	**Ottavia Bellotto**	*Supramolecular hydrogels from unprotected dipeptides: a comparative study on stereoisomers and structural isomers the Photocurrent Efficiency in a Peptide Supramolecular System*
16.30 - 17.00	**Break**		
17.00 - 17.30	**CSB PZ002**	**Claudia Bonfio**	*Uncovering the emergence of modern cells*
17.30 - 17.45	**CSB OR003**	**Gianantonio Battistuzzi**	*Molecular basis of myoglobinopathy, a newly discovered molecular disease*
17.45 - 18.00	**CSB OR004**	**Lidietta Giorno**	*Selectivity and stability of biological macromolecules heterogenized to nanostructured artificial membranes*

18.00 - 18.15	**CSB OR005**	**Claudia Riccardi**	*Design, synthesis and characterization of cyclic TBA analogues*
18.15 - 18.50	**Discussione**		

Divisione DIDATTICA CHIMICA (DID)
DID 01

15:00-16:00	**DID PL001**	**Jan Apotheker**	*Developments in chemistry education*
16:00-16:30	**DID IL001**	**Mariano Venanzi**	*Sustainable chemistry for a sustainable teaching. A proposal for a first level curriculum in Chemistry at University*
16:30-16:45	**DID OR001**	**Federica Branchini**	*Teaching the notion of chemical bonding: a didactic challenge*
16:45-17:00	**DID OR002**	**Maria Antonietta Carpentieri**	*A new didactic pathway to introduce Spectroscopy by historical-epistemiological/STEM laboratorial/distance learning blended approach*
17:00-17:15	**DID OR003**	**Maria Costa**	*Virtual Reality visualizations of complex molecular structures in chemistry education. The β-CD-ASA example*
17:15-17:30	**DID OR004**	**Sandro Jurinovich**	*A didactic sequence for teaching chromatography: observation, model and practical applications*
17:30-17:45	**DID OR005**	**Dora Stella Lombardi**	*'Light and Molecules': an experimental approach to the understanding of basic concepts of Quantum Mechanics*
17:45-18:00	**DID OR006**	**Alma Moretta**	*Additional Learning Requirements (OFA) in Math for Environmental Science degree course: a review for a better understanding of the difficulties of students entering university*
18:00-18:15	**DID OR007**	**Davide Peddis**	*From the astro to the nano scale: a learning by doing teaching pathway*
18:15-18:30	**DID OR008**	**Antonio Testoni**	*Chemistry, history and complexity*
18:30-18:45	**DID OR009**	**Sergio Palazzi**	*A colorful new morning - teaching applied chemistry in pandemic times*

Divisione SPETTROMETRIA DI MASSA (MAS)
MAS 01

15.00 - 15.15	**Welcome**		
15.15 - 15.55	**MAS PL001**	**Giuseppina Maccarone**	*The Role of Mass Spectrometry in the – omics Era*
15.55 - 16.10	**MAS OR001**	**Daniela Cecconi**	*Integrated lipidomics and proteomics reveal cardiolipin remodelling, upregulation of HADHA and long chain fatty acids in pancreatic cancer stem cells*
16.10 - 16.25	**MAS OR002**	**Silvia Pedretti**	*Metabolomic approaches to investigate the role of the mitochondrial*
16.25 - 16.35	**Break**		

15 settembre - pomeriggio

16.35 - 17.15	**MAS PL002**	**John A. McLean**	*High dimensional molecular phenomics in systems, synthetic, and chemical biology*
17.15 - 17.30	**MAS OR003**	**Isabella Piga**	*Spatial proteomics to map tissue alterations during the progression of fibrosis in an IPF and Nintedanib-treated mouse model*
17.30 - 17.45	**MAS OR004**	**Federico Fanti**	*Quantitative analysis of resolvins in biological matrices by means LLE-μSPE-HPLC-MS/MS*
17.45 - 18.00	**MAS OR005**	**Elettra Barberis**	*A Combined GCxGC-MS and GC-MS Approach to Discovery and Validate New Potential Biomarkers for Prostate Cancer Diagnosis*

Divisione TEORICA E COMPUTAZIONALE (TEO)

15:00 -15:20	**TEO KN001**	**Emilia Sicilia**	*Computations for investigating anticancer activity of metal-based compounds beyond cisplatin*
15:20 - 15:40	**TEO PZ001**	**Greta Donati**	*Exploring Chemistry through Multiple Time and Size Scales*
15:40 - 15:50	**TEO OR001**	**Marco Bertani**	*Improving empirical force fields for molecular dynamics simulations of oxide glasses. The importance of three-body interactions in rigid-ion models*
15:50 - 16:00	**TEO OR002**	**Arianna Massaro**	*First-principles study of Oxygen redox activity in P2-type NaxNi0.25Mn0.68O2 high energy cathode for Na-ion batteries*
16:00 - 16:10	**TEO OR003**	**Mirko Vanzan**	*An atomistic insight on the hot-electron injection mechanism*
16:10 - 16:20	**TEO OR004**	**Sergio Tosoni**	*Computational characterization of single-atom species on metal-supported oxide thin films*
16:20 - 16:30	**TEO OR005**	**Ida Ritacco**	*Spontaneous Production of Ultrastable Reactive Oxygen Species on Titanium Oxide Surfaces Modified with Organic Ligands*
16:30 - 17:00	**break**		
17:00 - 17:20	**TEO PZ002**	**Alessandro Erba**	*The Role of Fock Exchange in Relativistic Density Functional Theory*
17:20 - 17:30	**TEO OR006**	**Luca Brugnoli**	*Development and application of a ReaxFF Reactive Force Field for Cerium Oxide/Water Interfaces*
17:30 - 17:40	**TEO PO005**	**Anna Ranaudo**	*Computational study on the structural stability of mutated Affitins*
17:40 - 17:50	**TEO OR008**	**Noelia Faginas-Lago**	*Molecular Simulations of CO2/N2/H2O Gaseous Mixture Separation in Graphtriyne Membrane*
17:50 - 18:00	**TEO OR009**	**Francesca Fasulo**	*Electrode-electrolyte interface in solid-state lithium batteries: new insights from density functional embedding theory*

15 settembre - pomeriggio

18:00 - 18:10	**TEO OR010**	**Mariagrazia Fortino**	*Multi-replica biased sampling for photoswitchable p-conjugated polymers*
18:10 - 18:30	**discussion**		

Programma dei LAVORI di DIVISIONE - 16 settembre mattina

Divisione CHIMICA ANALITICA (ANA)

ANA 04

09.30 - 09.50	**ANA IL004**	**Cosima Damiana Calvano**	*Allergenicity assessment of novel foods by identifying marker peptides using bioinformatics and LC-ESI-MS/MS*
09.50 - 10.10	**ANA OR024**	**Danilo Corradini**	*Separation and Detection of Charged and Neutral Biomolecules in Plants and Food Matrices by Capillary Zone Electrophoresis*
10.10 - 10.15	**break**		
10.15 - 10.30	**ANA OR025**	**Antonella Cavazza**	*Analytical approaches for safety assessment in the development of innovative packaging solutions*
10.30 - 10.45	**ANA OR026**	**Tatiana Chenet**	*Evaluation of the presence of plastics in two fish species of the Mediterranean Sea and potentially correlated harmful effects*
10.45 - 11.00	**ANA OR027**	**Paola Arena**	*A Holistic Approach to the Characterization of High-Value Generating Molecules from the Wastes of Tuna Fishery Industry*
11.00 - 11.15	**ANA OR028**	**Federica Dal Bello**	*Insects food for the future*
11.15 - 11.30	**ANA OR029**	**Debora fabbri**	*Integrated approach for the analysis of some pesticides in vegetables and food matrices fastidiosa*
11.30 - 11.45	**ANA OR030**	**Paola Agata E. Donato**	*Triacylglycerol Fingerprinting in Vegetable Oils by means of Subcritical Solvent Chromatography*
11.45 - 12.00	**ANA OR031**	**Marco Iammarino**	*Exploring the potentiality of capillary ion chromatography (CIC) as analytical technique for the determination of food additives*
12.00 - 12.15	**ANA OR032**	**Fabio Salafia**	*Use of ultra-high performance liquid chromatography to characterize non-volatile compounds in Italian beers*
12.15 - 12.30	**ANA OR033**	**Emanuela Trovato**	*Characterization of volatile and non volatile compounds in citrus beer to evaluate product quality for food frauds prevention.*

ANA 05

09.30 - 09.50	**ANA KN004**	**Alessandra Biancolillo**	*Variable selection with a focus on multi-way and multi-block data*
09.50 - 10.10	**ANA KN005**	**Cristina Malegori**	*Near infrared hyperspectral imaging combined with multivariate image analysis: potential and limitations for the identification of microplastics in aquatic samples*
10.10 - 10.15	**break**		
10.15 - 10.30	**ANA OR034**	**Giacomo Baccolo**	*Automate chemometric approach for peak identification and quantification in untargeted GC-MS data*

10.30 - 10.45	**ANA OR035**	**Denise Biagini**	*Oxylipin storm in COVID-19: a new perspective in classifying disease severity*
10.45 - 11.00	**ANA OR036**	**Francesca Di Donato**	*Authentication of donkey's milk by Near Infrared Spectroscopy coupled with chemometric classifiers*
11.00 - 11.15	**ANA OR037**	**Fabio Fornari**	*Connecting the dots between theory and practice: discovering new functional cocrystals through supervised pattern recognition*
11.15 - 11.30	**ANA OR038**	**Sabina Licen**	*SOMEnv: an R package for mining environmental monitoring datasets by Self-Organizing Map and k-means algorithms with a Graphical User Interface*
11.30 - 11.45	**ANA OR039**	**Lisa Rita Magnaghi**	*Optode & Chemometrics: Milk Freshness at a Glance*
11.45 - 12.00	**ANA OR040**	**Elisa Robotti**	*Optimization of the process of anaerobic digestion of FORSU by experimental design techniques*
12.00 - 12.15	**ANA OR041**	**Giorgia Sciutto**	*A chemometric strategy to exploit the complementary information from a combined XRF-Vis-NIR hyperspectral imaging system*
12.15 - 12.30	**ANA OR042**	**Federica Turrini**	*'Specialty' or 'Gourmet' oils: a multivariate statistical approach for the rapid identification of their botanical species*

ANA 06

09.30 - 09.50	**ANA KN006**	**Serena Arnaboldi**	*Unconventional Electrochemical Approaches for the Direct Readout of Chiral Information*
09.50 - 10.10	**ANA KN007**	**Isacco Gualandi**	*Electrosynthesis of Layered Double Hydroxides for analytical applications*
10.10 - 10.15	**break**		
10.15 - 10.30	**ANA OR043**	**Riccarda Antiochia**	*Wearable electrochemical microneedles-based nanoporous gold sensor for real time catecholamine detection*
10.30 - 10.45	**ANA OR044**	**Paolo Inaudi**	*Solid state electrochemical behaviour and spin multiplicity in charge transfer co-crystals of DBTTF:F4TCNQ*
10.45 - 11.00	**ANA OR045**	**Andreas Lesch**	*Large-scale production of electroanalytical sensors by combined inkjet printing and light-induced synthesis of metal nanoparticles*
11.00 - 11.15	**ANA OR046**	**Antonella Miglione**	*Combined paper-based substrates for electrochemical detection of copper ions in serum*
11.15 - 11.30	**ANA OR047**	**Patrizia R. Mussini**	*Enantiomer discrimination in voltammetry in media of high structural order at the electrochemical interphase implemented with chirality*

11.30 - 11.45	**ANA OR048**	**Laura Pigani**	*Cannabinoids fast detection in real matrices: an electrochemical sensors' approach*
11.45 - 12.00	**ANA OR049**	**Angelo Tricase**	*Electrochemical Characterization of supramolecular structure in Self-Assembled Monolayers*
12.00 - 12.15	**ANA OR050**	**Martina Vizza**	*Specific ion effect in electrochemistry: the deposition of copper in the presence of different background electrolytes*

Divisione CHIMICA FISICA (FIS)

FIS 03

Enerchem I

09:30-10:00	**FIS KN003**	**Emanuela Gatto**	*Photocurrent Generation in Supramolecular Bio-Inspired Nanoarchitectures on Gold Surface*
10:00-10:15	**FIS OR025**	**Cristina Artini**	*A novel approach for the evaluation of the defect clusters content in doped ceria through in-situ high pressure x-ray diffraction*
10:15-10.30	**FIS OR026**	**Chiara Milanese**	*Super activated biochar for solid state hydrogen storage and supercapacitors preparation*
10:30-10.45	**FIS OR027**	**Emanuela Sartori**	*Emissive Layered Perovskite Nanocrystals*
10:45-11:00	**FIS OR028**	**Giovanni Di Liberto**	*Theoretical Description Semiconductors Interfaces: insights from DFT*
11:00-11.15	**break**		

Enerchem II

11:15-11.30	**FIS OR029**	**Vanira Trifiletti**	*Synthesis of bismuth-based hybrid perovskites for thermoelectrics*
11.30-11.45	**FIS OR033**	**Mariarosaria Tuccillo**	*Operando study of a cobalt free Li-rich layered oxide materials (LRLO) in a lithium cell*
11:45-12:00	**FIS OR031**	**Simone Sansoni**	*Laser ablation in solution for a more sustainable perovskite-based optoelectronics*
12:00-12:15	**FIS OR030**	**GianLuca Chiarello**	*Photothermocatalytic steam reforming of methanol for H2 production*
12:15-12.30	**FIS OR032**	**Annalisa Polo (Vincitrice del Premio Semerano)**	*Effects of Mo6+ doping on the performance of BiVO4 photoanodes for solar water oxidation*

FIS 04

Physical Chemistry for Environment I

09:30-10:00	**FIS KN004**	**Luigi Gentile**	*Ecofriendly Isolation of Cellulose from buckwheat chaff*
10:00-10:15	**FIS OR039**	**Vito Rizzi**	*From agricultural wastes to a resource: Kiwi Peels as recyclable adsorbent to remove emerging pollutants from water*

16 settembre - mattina

10:15-10.30	**FIS OR035**	**Giuseppina Anna Corrente**	*Hydrochemical study of the Turbolo basin: evaluation of the spatial and seasonal variation of surface water quality*
10:30-10.45	**FIS OR036**	**Vanessa Miglio**	*Silica Monolith for the Removal of Pollutants from Gas and Aqueous Phases*
10:45-11:00	**FIS OR037**	**Gabriele Mulas**	*Investigation of mechanochemically driven CO2 conversion over Olivine powders*
11:00-11.15	**break**		

Physical Chemistry for Environment II

11:15-11.30	**FIS OR038**	**Pier Luigi Gentili**	*Establishing a link between Chemistry and Complexity Science to promote Sustainability*
11.30-11.45	**FIS OR034**	**Sebastiano Campisi**	*Tin-functionalized hydroxyapatite as an “ecofriendly bridge” joining water remediation and air protection processes*
11:45-12:00	**FIS OR040**	**Paolino Caputo**	*Use of Food Substances as chemical additives in the industrial field*
12:00_12:15	**FIS OR041**	**Alessio Zuliani**	*Environmentally friendly ZnO/Castor oil polyurethane composites for the efficient gas-phase adsorption of acetic acid*
12:15-12.30	**FIS OR042**	**Antonio Tursi**	*Synthesis and Enhanced Capture Properties of a New BioMOF@SWCNT-BP: Recovery of the Endangered Rare Earth-Elements from Aqueous Systems*

FIS 05

Spectroscopic Applications I

09:30-10:00	**FIS KN005**	**Elena Groppo**	*Revisiting the use of probe molecules in the characterization of heterogeneous olefin polymerization catalysts by IR spectroscopy*
10:00-10:15	**FIS OR043**	**Giampaolo Marcolin**	*Solvent-dependent Characterization of Fucoxanthin through 2D Electronic Spectroscopy Reveals New Details on the Intramolecular Charge Transfer State Dynamics*
10:15-10.30	**FIS OR044**	**Alessandra Forni**	*Multiple prompt and long-lived emissions from solid state purely organic materials*
10:30-10.45	**FIS OR045**	**Rosachiara Antonia Salvino**	*NMR in chiral partially ordered media: a tool for achieving conformational traits of small flexible enantiomers in solution*
10:45-11:00	**FIS OR046**	**Nicola Peruffo**	*Selective Switching of Multiple Plexcitons in Colloidal Materials: Directing the Energy Flow at the Nanoscale*

Spectroscopic Applications II

11:15-11.30	**FIS OR047**	**Elisabetta Collini**	*The effect of hydrogen bonds on the ultrafast relaxation dynamics of a BODIPY dimer*
11.30-11.45	**FIS OR048**	**Francesca Martini**	*Structure and dynamics of “cool” organic pigments by solid state NMR*

16 settembre - mattina

11:45-12:00	**FIS OR049**	**Margherita Bolognesi**	*Bidimensional black Phosphorus: surface functionalization, heterostructures with organic molecules, applications*
12:00_12:15	**FIS OR050**	**Annamaria Panniello**	*BODIPY-functionalized Quantum dots platform for high efficiency FRET processes*
12:30-12:45	**FIS OR093**	**Eleonora Vottero**	*C-H terminations in activated carbons and related catalysts:an Inelastic Neutron Scattering spectroscopy and DFT study*

Divisione CHIMICA INDUSTRIALE (IND)

IND 02

Sessione congiunta con Gruppo Interdivisionale Catalisi

09.30 - 9.40	**IND OR012**	**Annalisa Sacchetti**	*Bio-oils valorization by selective catalytic hydrogenation: a comparison between batch and continuous flow systems*
9.40 - 9.50	**IND OR013**	**Alessandra Toso**	*Pd/CeO2 as Passive NOx Adsorbers: key properties and NOx adsorption mechanism*
9.50 - 10.00	**IND OR014**	**Sebastiano Campisi**	*A green route to the catalytic nitrous oxide decomposition by transition metal doped hydroxyapatites*
10.00 - 10.10	**IND OR015**	**Luca Consentino**	*Ce doped WO3-TiO2 cordierite monoliths for Selective Catalytic Reduction of NOx by NH3*
10.10 - 10.20	**IND OR016**	**Roberto Fiorenza**	*The solar photothermo-catalytic approach for the VOCs degradation and the subsequent CO2 conversion*
10.20 - 10.30	**IND OR017**	**Melissa Greta Galloni**	*Cu, Fe, and CuFe exchanged hydroxyapatites as eco-friendly catalysts for NH3-SCR reaction*
10.30 - 10.45	**Discussion**		
10.45 - 11.00	**break**		
11.00 - 11.20	**IND KN003**	**Pierdomenico Biasi**	*From University to Industry: examples on how university-industry collaborations in catalysis can be effective and successful*
11.20 - 11.30	**IND OR018**	**Fabiana Vento**	*Photodegradation of Xenobiotics from Polluted Water Using a New PMMA-TiO2 Based Nanocomposite*
11.30 - 11.40	**IND OR019**	**Vincenzo Russo**	*Heterogeneous photodegradation for the removal of ibuprofen from water*
11.40 - 11.50	**IND OR020**	**Alessandro Allegri**	*Aquivion® PFSA-based spray-freeze dried composite materials for the conversion of furfuryl alcohol to levulinates*
11.50 - 12.00	**IND OR021**	**Somayeh Taghavi**	*Biomass-derived levulinic acid hydrogenation to GVL using bifunctional biochar-based catalysts*
12.00 - 12.10	**IND OR044**	**Giulia Zoppi**	*Green hydrogen production from wastewater derived from lignin-rich hydrothermal liquefaction*
12.10 - 12.30	**Discussion**		

IND 03

09.30 - 9.50	**IND KN004**	**Michele Laus**	*Polymer brush technology: the true and the false in grafting to processes*
9.50 - 10.00	**IND OR023**	**Stefano Gazzotti**	*1,3-Dioxolan-4-Ones as powerful tool for the synthesis of functionalized PLA-based materials with tailored properties*
10.00 - 10.10	**IND OR024**	**Carla Calabrese**	*Hybrid organic-inorganic materials based on polydopamine-like chemistry*
10.10 - 10.20	**IND OR025**	**Alessandro Piovano**	*β-ketoimine Cr complexes for the production of functional polyolefins: exploring the metal-ligand bond as a key point of the catalysts*
10.20 - 10.30	**IND OR026**	**Edoardo Podda**	*Self-Healing and Shape-Memory Hydrogels by Micellar Polymerization*
10.30 - 10.40	**IND OR027**	**Riccardo Chiarcos**	*Evidence of Preferential Grafting of Short Chains in Grafting To Reactions of Hydroxy-Terminated P(S-r-MMA) Copolymers*
10.40 - 10.55	**Discussion**		
10.55 - 11.10	**break**		
11.10 - 11.20	**IND OR028**	**Antonietta Cozzolino**	*Axially oriented guest induced crystallization in syndiotactic polystyrene unstretched fiber*
11.20 - 11.30	**IND OR029**	**Manohar Golla**	*Axially Oriented Co-crystalline Phases of Poly(2,6-dimethyl-1,4-phenylene)oxide and host-guest orientations*
11.30 - 11.40	**IND OR030**	**Camilla Parmeggiani**	*Liquid crystal elastomer based artificial muscles for cardiac repair*
11.40 - 11.50	**IND OR031**	**Daniele Martella**	*Cell instructive polymers based on liquid crystals*
11.50 - 12.00	**IND OR032**	**Nicole Mariotti**	*Bio-based and waste-derived polyurethanes for energy systems*
12.00 - 12.30	**Discussion**		

Divisione CHIMICA ORGANICA (ORG)

ORG 05

10.00 - 10.30	**ORG PZ005**	**Marco Lucarini**	***Premio alla ricerca Chimica Organica nei suoi Aspetti Metodologici*** *Novel Spin-Labelled Mechanically Interlocked Molecules as Models for the Interpretation of Biradical EPR Spectra*
10.30 - 10.45	**ORG OR033**	**Fabio Buonsenso**	*Non-equilibrium dynamic chromatography: investigation of the reduction process of α-lipoic acid promoted by dithiothreitol*
10.45 - 11.00	**ORG OR034**	**Marta Da Pian**	*Combined use of forensic science in sexual assault: a case report*

11.00 - 11.15	**ORG OR035**	**Graziano Di Carmine**	*Aldol Reaction between Benzaldehyde and Hydroxyacetone Promoted by Silica SBA-15 supported proline: Unraveling the Solvent Effect on the Catalyst Behavior Using NMR Relaxation*
11.15 - 11.30	**ORG OR036**	**Elena Ermini**	*New 1-6 self-immolative spacer for the release of thiols under nitroreductase activation*

ORG 06

10.30 - 10.45	**ORG OR037**	**Germana Esposito**	*Molecular Networking: a powerful tool to dereplication of natural products*
10.45 - 11.00	**ORG OR038**	**Roberta Franzini**	*Chromatographic and spectroscopic investigation of chiral aza-dibenzocyclooctynes and their analogues obtained by azido-click reaction.*
11.00 - 11.15	**ORG OR039**	**Marco Galeotti**	*Hydrogen Atom Transfer based aliphatic C-H bond oxidation of hydrocarbons bearing cyclopropyl moieties. The role of hyperconjugation.*
11.15 - 11.30	**ORG OR040**	**Chiara Lambruschini**	*Photoisomerization of ferulic acid derivatives*

ORG 07

10.30 - 10.45	**ORG OR041**	**Francesca Ghirga**	*Development of ArnT-mediated colistin resistance diterpene-based inhibitors*
10.45 - 11.00	**ORG OR042**	**Laura Goracci**	*Exploring PROTACs metabolism: a structure-activity relationship study*
11.00 - 11.15	**ORG OR043**	**Concetta Imperatore**	*Toward marine inspired multitarget drugs for diabetes mellitus and its complications: design and synthesis of novel dual Protein Tyrosine Phosphatase 1B and Aldose Reductase ligands*
11.15 - 11.30	**ORG OR044**	**Marco Masi**	*Phytotoxins produced by fungal pathogens of legume crops*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 02

09.30 - 10.00	**CSB KN002**	**Paola Turano**	*Bioinorganic chemistry of ferritin nanocages*
10.00 - 10.15	**CSB OR006**	**Veronica Ghini**	*NMR as a tool to monitor the individual response of immunotherapy*
10.15 - 10.30	**CSB OR007**	**Luigi Russo**	*μs-ms conformational dynamics control the formation of prion protein intermediate states involved in amyloid fibrils*
10.30 - 10.45	**CSB OR008**	**Sabrina Elkhanoufi**	*New, highly sensitive off/on EPR probes to monitor enzymatic activity*
10.45 - 11.00	**CSB OR009**	**Alessia Distefano**	*A MS and SPR coupled approach to fully characterize IDE activity modulation*

11.00 - 11.15	**Break**		
11.15 - 11.30	**CSB OR010**	**Alessandro D'Urso**	*The increased thermodynamic stability of miRNAs might be the reason of stronger repressive activity*
11.30 - 11.45	**CSB OR029**	**Anna Di Porzio**	*Identification of a short peptide that preferentially binds to the G-quadruplex structure in the c-MYC oncogene promoter*
11.45 - 12.00	**CSB OR012**	**Chiara Platella**	*Targeting cancer-related DNA G-quadruplex structures by naphthalene diimide ligands*
12.00 - 12.15	**CSB OR013**	**Alessandra Romanelli**	*Self-assembly of PNA-peptide conjugates*
12.15 - 12.45	**Discussione**		

Divisione ELETTROCHIMICA (ELE)
ELE 04

09.30 - 10.00	**ELE IL28**	**Sara Rebeccani**	*PEDOT doped with Sulphonated Polyarylethersulphones as electroactive material in electroanalytical applications*
10.00 - 10.15	**ELE IL29**	**Cecilia Wetzl**	*Graphene-based functional materials for electrochemical imaging*
10.15 - 10.30	**ELE IL30**	**Lorenzo Ripani**	*Microkinetic modeling for the electrochemical CO2 reduction reaction in bicarbonate electrolyte*
10.30 - 10.45	**break**		
10.45 - 11.00	**ELE IL31**	**Riccardo Brandiele**	*Synthesis and characterization of materials for PEM-FC, based on Pt alloyed nanoparticles supported on next generation mesoporous carbon*
11.00 - 11.15	**ELE IL32**	**Annalisa Polo**	*Ternary Oxide Semiconductor Photoanodes for Solar Energy Conversion*
11.15 - 11.45	**ELE IL33**	**Laura Rotundo**	*Electroreduction of carbon dioxide by Re(I) and Mn(I) bipyridine complexes*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)
TEC 03

9.30 - 9.40	**TEC OR025**	**Paola Di Matteo**	*Phenolic compounds in alcoholic and low-alcoholic beer by fast HPLC-PDA-MS/MS analysis: impact of malt composition, hops and dealcoholization process.*
9.40 - 9.50	**TEC OR026**	**Elhussein M. F. M. H. Ahmed**	*Early-Detection of Xylella fastidiosa in Olive Trees by Hyperspectral Reflectance and Non-targeted Metabolomics*
9.50 - 10.00	**TEC OR027**	**Nazeeha Ayaz**	*Hydrophobin coated superfluorinated nanoparticles for 19F-MRI cell tracking*
10.00 - 10.10	**TEC OR028**	**Elena Dilonardo**	*S-PEEK membranes optimized for Vanadium Redox Flow Battery: the effects of sulphonation degree and filler content on operative conditions and set-up configurations*

16 settembre - mattina

10.10 - 10.20	**TEC OR029**	**Giuseppe Marcì**	*Selective photocatalytic partial oxidation of aromatic alcohols to aldehydes in aqueous suspensions of C3N4 obtained by polycondensation of melamine and cyanuric/barbituric acids*
10.20 - 10.40	**Discussion**		
10.40 - 10.50	**TEC OR030**	**Giancarlo Terraneo**	*Crystalline Molecular Rotors Assembled through Halogen Bonding*
10.50 - 11.00	**TEC OR031**	**Valentina Dichiarante**	*Multi-branched perfluoro-tert-butoxyl scaffolds for the functionalization of surfaces and nanomaterials*
11.00 - 11.10	**TEC OR032**	**Gabriella Munzi**	*A dinuclear Zn(II) Schiff-base complex as molecular tweezer: binding properties and sensing towards biogenic diamines*
11.10 - 11.20	**TEC OR033**	**Martina Lippi**	*Dynamic 1D Bispidine-based Coordination Polymers for Adsorption Applications*
11.20 - 11.30	**TEC OR034**	**Daniele Narzi**	*Mechanism of oxygen evolution and Mn4Ca cluster restoration in the natural water-oxidizing catalyst*
11.30 - 11.50	**Discussion**		

Programma dei LAVORI di DIVISIONE - 17 settembre mattina

Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

ABC 02

09.30-10.00	**ABC KN001**	**Edith Joseph**	*Green methods for metals conservation*
10.00-10.15	**ABC OR023**	**Francesco Abate**	*The evolving perspective on the study of ancient bronze coins*
10.15-10.30	**ABC OR024**	**Cecilia Velino**	*Investigation of the corrosive effects of ambient particulate matter on bronze through accelerated sampling and ageing*
10.30-10.45	**ABC OR025**	**Maria Labate**	*The leading role of diagnostics for cultural heritage in historic studies and conservation: Sarezzano reliquary busts as a case study*
10.45-11.00	**ABC OR026**	**Andrea Timoncini**	*Characterization of bacteria community on bronze and marble statues*
11.00-11.15			
11.15-11.30			
11.30-11.45	**ABC OR027**	**Roberta Zanini**	*Laser Ablation ICP-MS elemental imaging to investigate corroded surfaces of ancient glass*
11.45-12.00	**ABC OR028**	**Lucrezia Gatti**	*A new analytical strategy for the characterization of diagenetic pathways in ancient bones and teeth.*
12.00-12.15	**ABC OR029**	**Raffaella Lamuraglia**	*Archaeometric investigation on Roman frescoes from the archaeological site of Aquileia*
12.15-12.30	**ABC OR030**	**Francesca Porpora**	*Diammonium hydrogen phosphate and Ca (OH)2 nanoparticles for consolidation of ancient bones: evaluation of performances*
12.30-12.45	**ABC OR052**	**Serena Spadavecchia**	*Evaluation of the effectiveness of coatings for the protection of outdoor terracotta artworks through artificial ageing*
12.45-13.00	**ABC OR032**	**Giulia C. Lodi**	*The assessment of the organic composition of historical remedies and drugs through a multidisciplinary approach*

ABC 03

09.30-09.45	**ABC OR034**	**Antonino Fiorentino**	*New photo-Fenton like process for roof harvested rainwater disinfection*
09.45-10.00	**ABC OR035**	**Elisa Gaggero**	*Removal of contaminants of emerging concern by enzymatic treatment with fungal laccases*
10-10.15.00	**ABC OR036**	**Giulia Guerra**	*Zinc and Iron Based Metal-Organic Frameworks as Ofloxacin Adsorbents in Polluted Waters*
10.15-10.30	**ABC OR037**	**Giuseppe Mascolo**	*Biodegradability enhancement of non-ionic surfactants in industrial wastewater by UV/H2O2 pre-treatment*

17 settembe - mattina

10.30-10.45	**ABC OR038**	**Giuseppe Mascolo**	*Remediation of groundwater contaminated with PCBs and PAHs by photocatalysis employing nano-sized TiO2* *supported onto steel mesh*
10.45-11.00	**ABC OR039**	**Mirco Volanti**	*Biogas to Syngas through the Combined Steam/Dry Reforming Process: An Environmental Impact Assessment*
11.00-11.15			
11.15-11.30			
11.30-11.45	**ABC OR040**	**Sapia Murgolo**	*Assessment of a sustainable biofilter technology for reducing the environmental spread of CECs and odour emissions*
11.45-12.00	**ABC OR041**	**Federica Piras**	*Vacuum-UV as pre- and post-treatment to biofiltration: a novel integrated treatment scheme for wastewater reuse*
12.00-12.15	**ABC OR042**	**Concetta Pironti**	*A study of the biocidal effectiveness of permaleic acid (PMA): new promising application in disinfection process*
12.15-12.30	**ABC OR043**	**Annarosa Gugliuzza**	*2D Materials Engineered Membranes for a New Vision on Water Desalination*
12.30-12.45	**ABC OR044**	**Giuseppe Vitola**	*Membrane biofunctionalization for pesticide removal in surface water and vegetative water*
12.45-13.00	**ABC OR045**	**Domenico Cipriano**	*Protocol implementation of odour Proficiency Tests (PTs)*

Divisione CHIMICA FARMACEUTICA (FAR)

FAR 05

09.30 - 10.00	**FAR KN005**	**Yimon Aye**	*Leveraging precision electrophile signaling toward drug discovery*
10.00 - 10.30	**FAR KN006**	**Antimo Gioiello**	*Enabling synthesis and technologies to develop bile acid-* *inspired lead compounds*
10.30 - 10.45	**FAR OR019**	**Francesca Ferlenghi**	*A sulfonyl fluoride derivative selectively inhibits EGFRL858R/T790M/C797S by covalent modification of the catalytic lysine*
10.45 - 11.00	**FAR OR020**	**Angelica Artasensi**	*Novel potential DPP IV/ CA II inhibitors for the treatment* *of Type 2 Diabetes*
11.00 - 11.30	**FAR KN007**	**Andrea Stevenazzi**	*The selective inhibition of histone deacetylase 6 (HDAC6)*
11.30 - 11.45	**FAR OR023**	**Giannamaria Annunziato**	*Investigational studies on cyclopropane− carboxylic acid* *derivatives targeting O acetylserine sulfhydrylase as colistin adjuvants*
11.45 - 12.00	**FAR OR024**	**Simone Lucarini**	*Phenotype screening of a bisindole chemical library identifies URB1483 as a new antileishmanial agent with topoisomerase IB as molecular target*

12.00 - 12.15	**FAR OR025**	**Santo Previti**	*Development of peptidyl Michael acceptors for S3 pocket investigation of rhodesain, cysteine protease of Trypanosoma brucei rhodesiense*
12.15 - 12.30	**FAR OR026**	**Valentina Straniero**	*Development of benzodioxane-benzamides inhibitors of FtsZ as potent broad-spectrum antimicrobial agents*
12.30 - 13.00	**FAR KN008**	**Anna K.H. Hirsch**	*Addressing underexplored anti-infective targets*

FAR 06

10.30 - 10.45	**FAR OR021**	**Maria Dichiara**	*Design, synthesis and pharmacological evaluation of 4-carbamothioylphenyl sigma-1 receptor antagonists for pain treatment*
10.45 - 11.00	**FAR OR022**	**Giacomo Rossino**	*Identification of novel Sigma 1 receptor antagonists based on arylalkanolamine scaffold for the treatment of neuropathic pain*
11.00 - 11.30			
11.30 - 11.45	**FAR OR027**	**Marilena Muraglia**	*To042: prospective lead compound for the treatment of myotonic syndromes*
11.45 - 12.00	**FAR OR028**	**Sebastiano Intagliata**	*Development of mutual prodrugs of 5-fluorouracil and heme oxygenase 1 inhibitor as anticancer agents*
12.00 -12.15	**FAR OR029**	**Luca Pinzi**	*LigAdvisor: a web server to perform in silico explorations on crystallographic ligands and known drugs for polypharmacology and drug repurposing*
12.15 -12.30	**FAR OR030**	**Lucilla Turco**	*NMR contributions to process chemistry sustainability in the pharmaceutical research area*

Divisione CHIMICA FISICA (FIS)

FIS 06

Physical Chemistry for Biomedical Applications III

09:30-10:00	**FIS KN006**	**Debora Scuderi**	*Free electron Laser and IRMPD spectroscopy*
10:00-10:15	**FIS OR052**	**Rita Gelli**	*Insights into biologically-relevant calciprotein particles: effect of stabilizing agents on the formation and crystallization mechanisms*
10:15-10.30	**FIS OR053**	**Alessandra Del Giudice**	*Regulation of the photosynthetic AB-GAPDH via self-assembly*
10:30-10.45	**FIS OR054**	**Davide Tocco**	*Investigation of Fe-BTC and Z MOFs as carrier for Aspergillus.sp Laccase*
10:45-11:00	**FIS OR055**	**Pasquale Sacco**	*Biopolymer-based platforms for cell mechanosensing and regenerative medicine*

11:00-11.15	**FIS OR057**	**Marta Penconi**	*Advancing near-IR phosphorescence with Ir(III) complexes bearing a single emitting ligand: properties and OLED applications*
11.15-11.45	**break**		

Sessione congiunta con TEO

11:45-12:00	**FIS OR058**	**Fabio Gabas**	*Divide and Conquer Semiclassical Initial Value Representation: a valuable theoretical tool for vibrational spectroscopy of biological systems*
12:00_12:15	**TEO OR011**	**Giacomo Saielli**	*A computational view of ionic liquid crystals*
12:15-12.30	**FIS OR060**	**Tommaso Giovannini**	*Energy-Based Molecular Orbital Localization in specific Molecular Regions*
12:30-12:45	**TEO OR012**	**Alessio Petrone**	*Electronic attosecond dynamics: Ab initio treatment of photo-induced excitonic states*
12:45-13:15	**FIS KN007**	**George Froudakis**	*Designing Novel Nanoporous Materials for Applications in Energy and Environment. From Multi-Scale Modeling to Materials Informatics*

FIS 07

Sessione congiunta con CSB

09:30-10:00	**FIS KN008**	**Roland Winter**	*Temperature, Pressure, and Cosolute Effects on Liquid–Liquid Phase Separation and Condensates of Proteins: Physical Chemistry and Biological Implications*
10:00-10:15	**FIS OR067**	**Francesca Baldelli**	*Superfluorinated Exosomes for Sensitive in Vivo Tracking by 19F-MRI*
10:15-10.30	**FIS OR063**	**Cristina Carucci**	*Drug loaded polymer coated silica nanoparticles as drug delivery route against bacteria*
10:30-10.45	**FIS OR064**	**Francesca Biscaglia**	*Engineered Peptides on Gold Nanostructures for Enhanced Targeting Activity in Cancer Diagnosis*
10:45-11:00	**FIS OR065**	**Ilaria Clemente**	*Cubic and lamellar mesophases obtained from algal biomass as drug carriers with high potentiality*
11:00-11.15	**CSB OR026**	**Angelo Spinello**	*Small-molecule modulators of spliceosome-mutant cancers as a new therapeutic strategy against hematologic malignancies*
11:15-11.30	**CSB OR027**	**Nunzia Iaccarino**	*Effects of sequence and base composition on the CD and TDS profiles of i DNA*
11.30-11.45	**break**		

Sessione congiunta con ELE

11:45-12:15	**FIS KN009**	**Maria Vittoria Dozzi**	*CuWO4-based photoanodes for solar energy conversion: effects of Mo6+ doping and coupling with BiVO4*
12:15-12:30	**ELE OR038**	**Gennaro Sannino**	*Development of SnO2 composites as electron transport layer in un-encapsulated CH3NH3PbI3 solar cells*

12:30-12:45	**FIS OR069**	**Guillermo Escolano Casado**	*Cu-functionalized hydroxyapatites: a study of their physico-chemical properties and their potential as electrocatalysts*
12:45-13:00	**ELE OR039**	**He Xiufang**	*Investigation of the mechanism of Pt3Fe3 clusters for the hydrogen evolution reaction and for the oxygen reduction reaction*
13:00-13:15	**FIS OR071**	**Simone Di Muzio**	*Thermodynamics of the hydrolysis of lithium salts: pathways to the inorganic SEI components*

Divisione CHIMICA INORGANICA (INO)

INO 04

9.30 - 9.50	**INO PZ002 (Premio Dottorato 2020)**	**Anna Dall'Anese**	*Palladium catalyzed copolymerizations: from ligand architecture to macromolecule microstructure*
9.50 - 10.10	**INO PZ003 (Premio Dottorato 2020)**	**Giacomo Picci**	*Novel supramolecular architectures based on weak interactions*
10.10 - 10.30	**INO PZ004 (Premio Dottorato 2020)**	**Fortuna Ponte**	*Anticancer drugs: a detailed computational analysis of “non classical” compounds mechanism of action*
10.30 - 10.45	**INO OR022**	**Andrea Biffis**	*Gold catalyzed direct alkyne hydroarylations in ionic liquids: a powerful tool in organic synthesis*
10.45 - 11.00	**INO OR023**	**Luca Conti**	*Ru(II) polypyridyl complexes as promising light-responsive agents for biological application*
11.00 - 11.15	**INO OR024**	**Filippo Campagnolo**	*Development of sustainable and green methodologies for homogeneous gold(I) catalysis*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR025**	**Matteo Atzori**	*Magneto-chiral dichroism in chiral molecular magnets*
11.45 - 12.00	**INO OR026**	**Stefano Scoditti**	*Anticancer and photophysical properties of a N^C^N-coordinated Pt(II) complex*
12.00 - 12.15	**INO OR027**	**Paolo Cleto Bruzzese**	*17O spin density studies of single-metal sites in Cu-CHA zeolites*
12.15 - 12.30	**INO OR028**	**Federica Santulli**	*A single catalyst for the synthesis and chemical depolymerization of polylactide*
12.30 - 13.00	**INO PZ005 (Premio Nasini 2020)**	**Enrico Ravera**	*Paramagnetic NMR in bioinorganic chemistry in the ‘twenties*

INO 05

10.30 - 10.45	**INO OR029**	**Mauro Ravera**	*Pt(IV) bifunctional complexes as anticancer agents: “is this true glory?”*

10.45 - 11.00	**INO OR030**	**Alessia Giordana**	*Solid acid catalysts for glucose hydrolysis: quantification of Lewis and Brønsted acid sites using 2,6-dimethylpyridine*
11.00 - 11.15	**INO OR031**	**Giorgio Facchetti**	*New sp3 diphosphine-based rhodium catalysts for the asymmetric addition of aryl boronic acids to azaarenes*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR032**	**Marco Chino**	*Design of a miniaturized FeS4 protein*
11.45 - 12.00	**INO OR033**	**Paolo Centomo**	*Selectivity enhancement of coordinating solvents on the direct synthesis of hydrogen peroxide*
12.00 - 12.15	**INO OR034**	**Tania Pecoraro**	*Luminescent self-assemblies of Pt(II) complexes in vivo*
12.15 - 12.30	**INO OR035**	**Cristiana Cesari**	*Homometallic and heterometallic ruthenium hydride carbonyl cluster*

INO 06

10.30 - 10.45	**INO OR036**	**Andrea Rossin**	*Thiazole-based Metal-Organic Frameworks for applications in CO2 storage/utilization and luminescence sensing*
10.45 - 11.00	**INO OR037**	**Patrizio Campitelli**	*Amino-decorated zinc bipyrazolate MOFs, an example of carbon dioxide capture and reuse (CCR)*
11.00 - 11.15	**INO OR038**	**Giorgio Tseberlidis**	*Sol-gel deposition of Cu2XYS4 thin-films with tunable bandgap as absorbers for photovoltaic applications*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR039**	**Francesca Deganello**	*Recycling inorganic waste into sustainable materials for energy and environment*
11.45 - 12.00	**INO OR040**	**Damiano Ricciarelli**	*Energy vs charge transfer in manganese doped lead halide perovskites*
12.00 - 12.15	**INO OR041**	**Marco Bellini**	*Electrocatalysis for energy: from nanostructured to molecular approach*
12.15 - 12.30	**INO OR042**	**Chiara Domestici**	*Novel mononuclear and dinuclear Ir-Cp* complexes bearing phosphonate and carboxylate ancillary and anchoring ligands as homogeneous and heterogenized water oxidation catalysts*

Divisione ELETTROCHIMICA (ELE)

ELE 05

09.30 - 10.00	**ELE_KN34**	**Matteo Bonomo**	*NiO/ZrO2 nanocomposites as photocathodes of tandem DSCs with higher photoconversion efficiency with respect to parent single-photoelectrode p-DSCs*
10.00 - 10.15	**FIS_OR068**	**Giuseppe Arrabito**	*Inkjet Printing Quasi-Miscible Droplets for Pseudo-Planar Organic Heterojunctions*
10.15 - 10.30	**ELE_OR35**	**Alessandro Facchin**	*Oxygen Reduction Reaction monitoring at Iron Single Site Catalyst: Electrochemical Scanning Tunnelling Microscopy of Iron Octaethylporphyrin*
10.30 - 10.45	**FIS_OR070**	**Mariangela Curcio**	*Laser irradiation of Bio-waste derived carbon as anode for Li-ion batteries*

10.45 - 11.00	**ELE_OR36**	**Barbara Vercelli**	*Doping or Aggregation: the case of Conjugated Polyelectrolytes PCPDTBT-2SO3K and PCPDTBT-SO3K*
11.00 - 11.15	**FIS_OR130**	**Elena Messina**	*Electrochemical study of Smart Nanocarriers forImproved Corrosion Protection of Reinforced Concrete*
11.15 - 11.30	**ELE_OR37**	**Marco Malferrari**	*Light-Induced Electrochemical Processes at Semiconductor-Films/Water Interface Modulate Cell Redox Balance*

ELE 06

09.30 - 10.00	**ELE_KN40**	**Stefania Rapino**	*Cancer Metabolic Profile Detected by Scanning ElectroChemical Microscopy*
10.00 - 10.15	**ANA_OR137**	**Ilaria Ragazzini**	*A simple and industrially scalable method for making a PANI-modified cellulose touch sensor*
10.15 - 10.30	**ELE_OR42**	**Nikolaou Pavlos**	*Ultrasensitive Hepatitis B Virus whole genome detection by Electrochemiluminescence*
10.30 - 10.45	**ANA_OR136**	**Cosimino Malitesta**	*Electrosynthesised ion imprinted polymers in development of sensor for Cd(II) ions determination in water*
10.45 - 11.00	**ELE_OR44**	**Patrik Sfragano**	*A bicyclic peptide-based biosensor for the electrochemical detection of a cancer-related protease*
11.00 - 11.15	**ANA_OR134**	**Veronica Caratelli**	*A Paper-Based Electrochemical Device for the Detection of Pesticides Inspired by Nature: a Flower-Like Origami Biosensor*
11.15 - 11.30	**ELE_OR43**	**Silvia Comis**	*Determination of emerging contaminants with electrochemical sensors based on titania nanoporous films: effect of sol aging on their electrochemical performances*
11.30 - 11.45	**break**		
11.45 - 12.00	**ANA_OR135**	**Noemi Colozza**	*A multiparametric electrochemical device for degradation monitoring in reinforced concrete*
12.00 - 12.15	**ELE_OR41**	**Alessanra Zanut**	*DNA-based Nanoswitches: insights into electrochemiluminescence signal enhancement*

ELE 07

11.30 - 12.00	**ELE_KN045**	**Marta Feroci**	*Solvent-supporting electrolyte system in electrolysis: not only chemical environment and charge carrier*
12.00 - 12.15	**ELE_OR04 6**	**Angeloclaudio Nale**	*Interplay between porosimetric parameters, densitometric parameters and catalytic activities of “Core-Shell” ORR Electrocatalysts*
12.15 - 12.30	**ELE_OR047**	**Gioele Pagot**	*Ion Coordination and Dynamics in Ionic Liquid-based Electrolytes for Hybrid Al/Mg Batteries*
12.30 - 12.45	**ELE_OR048**	**Carpanese Maria Paola**	*Copper-based perovskite electrodes for reversible solid oxide cells*
12.45 - 13.00	**ELE_OR049**	**Duranti Leonardo**	*Multi-functional Fuel Electrode for Reversible Solid Oxide Cells*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)

TEC 04

17 settembe - mattina

9.30 - 10.00	**TEC IL002**	**Lvova Larisa**	*Recent advances in potentiometric sensors for environmental purposes: from single ion-selective electrodes to multisensor analysis*
10:00 - 10:10	**TEC OR035**	**Moulaee Kaveh**	*A new electrochemical platform for fast and efficient determination of dominant non-psychoactive cannabinoids in Cannabis Sativa*
10:10 - 10:20	**TEC OR036**	**Ferlazzo Angelo**	*Crown ether functionalized graphene quantum dots as electrochemical and fluorescence based sensors for the selective detection of potassium and sodium ions*
10:20 - 10:30	**TEC OR037**	**Zribi Rayhane**	*Electrochemical and sensing properties of 2D-MoS2 nanosheets produced via liquid cascade centrifugation at different rate*
10:30 - 10:40	**TEC OR038**	**Bella Federico**	*Hybrid solar cells operating in aqueous environment*
10:40 - 10:50	**TEC OR039**	**Grisorio Roberto**	*A new synthetic approach for size-tunable and stable CsPbBr3 nanocubes with near-unity photoluminescence quantum yield*
10:50 - 11:00	**TEC OR040**	**Bortolami Martina**	*BMIm-BF4: a versatile ionic liquid for BF3 generation and reactions*
11:00 - 11:15	**Discussion**		

Divisione TECNOLOGIA FARMACEUTICA (TFA)
TFA 02

09.30 - 10.00	**TFA IL003**	**Mauro Bonini**	*Release in oral solid nutraceutical forms: case studies.*
10.00 - 10.30	**TFA IL004**	**Marco Fidaleo**	*A lesson from Vitamin B12: from the biological issues to the design of a nutraceutical formulation*
10.30 - 10.45	**Discussion**		
10.45 - 11.00	**break**		
11.00 - 11.15	**TFA OR010**	**Annalisa Bianchera**	*Crystallization of stable doped mannitol polymorphs and in vitro assessment of their safety as carriers for lung delivery*
11.15 - 11.30	**TFA OR011**	**Luca Casula**	*Multicomponent nanosuspension for the bronchial asthma inhalation therapy*
11.30 - 11.45	**TFA OR012**	**Luca Cerri**	*Spray patch based on hyaluronic acid and chitosan microparticles medicated with olive leaf extract*
11.45 - 12.00	**TFA OR013**	**Maria Chiara Cristiano**	*EtoGel: combined systems for new ethosomes application in joint diseases treatments*
12.00 - 12.15	**TFA OR014**	**Tiziana Esposito**	*Castanea sativa waste as dermo-functional ingredient into a topical delivery system: from the design and development of the formulation to in vitro stability and in vivo skin tolerability and efficacy*
12.15 - 12.30	**TFA OR015**	**Diego R. Perinelli**	*Development of topical formulations using hydrolyzed keratin as an alternative to the commonly employed emulsifying agents*

17 settembe - mattina

12.30 - 12.45	**TFA OR016**	**Teresa Silvestri**	*Biodegradable microparticles for the treatment of the posterior eye segment diseases*
12.45 - 13.00	**TFA OR017**	**Elena Giuliano**	*Poloxamer– and poloxamine-based hydrogels as biocompatible systems for the delivery of active compounds*
13.00 - 13.15	**TFA OR018**	**Umberto M. Musazzi**	*Printing of cutaneous patches loaded with propranolol for the treatment of infantile hemangiomas*

Programma dei LAVORI di DIVISIONE - 17 settembre pomeriggio

Divisione CHIMICA ANALITICA (ANA)

ANA 07

15.00 - 15.20	**ANA PZ003**	**Mariosimone Zoccali**	*Is There a Real Need for Multidimensional Chromatography Strategies with the Current Availability of Powerful Mass Spectrometry Platforms?*
15.20 - 15.40	**ANA KN008**	**Giovanni Ventura**	*AllerT: a Matlab-based workflow for putative allergens identification in novel foods via LC-ESI-MS/MS analysis*
15.40 - 16.00	**ANA OR051**	**Domenica Mangraviti**	*Differentiation and profiling of Morocco species belonging to Lamiaceae Family by Ambient Mass Spectrometry methods*
16.00 - 16.15	**ANA OR052**	**Nicole Marittimo**	*Advancements in Direct-MS using SPME coupled to Liquid-EI and CI*
16.15 - 16.30	**ANA OR053**	**Katia Arena**	*Characterization of bioactive compounds from natural products using focusing-modulated comprehensive two-dimensional liquid chromatography coupled to mass spectrometry*
16.30 - 16.45	**ANA OR054**	**Eleonora Oliva**	*Analysis of phenolic compounds in plant matrices by means of HPLC-MS/MS with targeted and semi-untargeted approach*
16.45 - 17.00	**ANA OR055**	**Tania Salerno**	*The Coupling of Gas Chromatography - Mass Spectrometry with Infrared Spectroscopy for Reliable Identification of Unknowns in Complex Samples*
17.00 - 17.15	**ANA OR056**	**Danilo Sciarrone**	*Reliability of monodimensional vs multidimensional GC-C-IRMS data: a critical evaluation*
17.15 - 17.30	**ANA OR057**	**Peter Q. Tranchida**	*Options of 1D GC, flow-modulation signal-enhanced 1D GC and flow-modulation comprehensive 2D GC in a single instrument: a proof-of-concept study*
17.30 - 17.45	**ANA OR058**	**Cecile Valsecchi**	*Enhanced LC-MS/MS spectra matching through multi-task neural networks and molecular fingerprints*

ANA 08

15.20 - 15.40	**ANA IL005**	**Alessandra Bianco Prevot**	*Organic Pollutant Removal using Photo-Fenton Processes in the presence of Fe(III) complexing agents*
15.40 - 16.00	**ANA IL006**	**Paola Fermo**	*In-situ and micro-destructive investigation for the analysis of degradation products present on marble surfaces*
16.00 - 16.15	**ANA OR059**	**Francisco Ardini**	*Evaluation of potential source areas for atmospheric lead reaching Ny-Ålesund (Svalbard) from 2010 to 2019*
16.15 - 16.30	**ANA OR060**	**Stefano Bertinetti**	*Strontium isotopic analysis of microsamples by inductively coupled plasma - tandem mass spectrometry*

16.30 - 16.45	**ANA OR061**	**Luca Carena**	*Photochemistry of furfuryl alcohol in/on snow at -30°C: photoreactivity with singlet oxygen and by direct photolysis*
16.45 - 17.00	**ANA OR062**	**Silvia Illuminati**	*Year-round records of bulk aerosol composition over the Victoria Land (Antarctica)*
17.00 - 17.15	**ANA OR063**	**Elisa Calà**	*Identification of aloe and other dyes by means of SERS and HPLC-DAD-MS in the embroidery of a 15th century English folded almanac*
17.15 - 17.30	**ANA OR064**	**Emilio Catelli**	*Rediscovering the lost color. Advanced vector quantization algorithm and hyperspectral imaging for digital restoration of color films*
17.30 - 17.45	**ANA OR065**	**Giovanna Marussi**	*The Third-Century monetary crisis: chemical analysis of Denarii and Antoniniani*
17.45 - 18.00	**ANA OR066**	**Rosaria Anna Picca**	*Synthesis and spectroscopic characterization of synergistic nanomaterials for stone artwork protection*

ANA 09

15.20 - 15.40	**ANA KN009**	**Paolo Bollella**	*Enzyme based Amperometric Biosensors: From Direct Electron Transfer to Chimeric Enzymes*
15.40 - 16.00	**ANA OR067**	**Giuseppe Arrabito**	*Printing Biology: engineering analytical platforms by molecular inks*
16.00 - 16.15	**ANA OR068**	**Noemi Bellassai**	*Design of dual-functional polymer on plasmonic biosensor for detection of circulating tumor DNA point mutations*
16.15 - 16.30	**ANA OR069**	**Alessandro Bertucci**	*Artificial Biomolecular Communication Regulated by Synthetic DNA Translators*
16.30 - 16.45	**ANA OR070**	**Alessandra Maria Bossi**	*Soft molecularly imprinted nanoparticles for protein recognition in sensing and assays*
16.45 - 17.00	**ANA OR071**	**Stefano Cinti**	*A microfluidic paper-based chip patterned with Prussian Blue to determine sweat urea*
17.00 - 17.15	**ANA OR072**	**Erica Del Grosso**	*Transient control of DNA-based systems*
17.15 - 17.30	**ANA OR073**	**Marco Giannetto**	*Smart immunosensors for point-of-care serologic test to determine the level of immunity by Covid-19 infection or by SARS-CoV-2 vaccination*
17.30 - 17.45	**ANA OR074**	**Antonia Lopreside**	*Reagent-free paper biosensor based on genetically modified bioluminescent protein for cancer biomarker detection*
17.45 - 18.00	**ANA OR075**	**Lucia Sarcina**	*Selective detection of Xylella fastidiosa with a Surface Plasmon Resonance based immunoassay*

Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

ABC 04

15.00-15.15	**ABC OR051**	**Dominique Scalarone**	*CAPuS project: research and higher education allied for the Conservation of Art in Public Spaces*

15.15-15.30	**ABC OR013**	**Ilaria Serafini**	*Advances in analytical methodologies applied to cultural heritage: first application of DLLME to characterize dyes in ancient textiles*
15.30-15.45	**ABC OR014**	**Slimani Sawssen**	*Caput Mortuum purple hematite pigment: Investigation of magnetic properties*
15.45-16.00	**break**		
16.00-16.15	**ABC OR015**	**Andrea Brunelli**	*Colloidal behavior of titanium dioxide nanoparticles in artificial and in Venice lagoon waters in the presence of standard or natural colloidal particles*
16.15-16.30	**ABC OR016**	**Felice Simeone**	*Assessment of the Cytotoxicity of Metal oxide Nanoparticles on the Basis of Immediately Available Physical-Chemical Parameters.*
16.30-16.45	**ABC OR017**	**Cristina De Ceglie**	*The effect of a karst-fractured aquifer on wastewater quality: an UHPLC-HRMS study*
16.45-17.00	**ABC OR018**	**Francesco Saliu**	*Plastic and its associated contaminants: determination of PAEs in coral reef invertebrates by in vivo SPME-LC-MS/MS*
17.00-17.15			
17.15-17.30	**ABC OR019**	**Armando Zarrelli**	*Characterization of degradation byproducts of Sartans: elucidation of their degradation pathway and ecotoxicity assessment*
17.30-17.45	**ABC OR020**	**Marco Mantovani**	*Microalgal treatment of the liquid fraction from hydrothermal carbonization process (HTC) in a circularity perspective*
17.45-18.00	**ABC OR021**	**Giulia Guidotti**	*Poly(diethylene 2,5-furanoate): a biobased promising candidate for compostable high-performant packaging*
18.00-18.15	**ABC OR022**	**Valeria D’Ambrosio**	*Lipids extraction from sewage sludge using green biosolvent for a sustainable production of biodiesel*

Divisione CHIMICA INDUSTRIALE (IND)

IND 04

Sessione congiunta con Gruppo Interdivisionale Energie Rinnovabili - Enerchem

15.00 - 15.30	**IND KN005 Chini Lecture**	**Carlo Perego**	*CO2 utilization: from waste to resource*
15.30 - 15.40	**IND OR033**	**Martina Serafini**	*Nanostructured Cu-based Electrocatalysts on a Carbonaceous Gas Diffusion Layer for the Electrochemical Reduction of CO2*
15.40 - 15.50	**IND OR034**	**Simelys Hernandez**	*How to exploit thermochemical catalysts to make efficient & sustainable CO2 electroreduction to added value products*
15.50 - 16.00	**IND OR035**	**Ivan Grigioni**	*High rate CO2 electroreduction to formate with a InP colloidal quantum dots derived catalyst*
16.00 - 16.10	**IND OR036**	**Federico Bella**	*Preliminary investigation of anodic materials for potassium batteries*
16.10 - 16.20	**IND OR037**	**Maria Grazia Musolino**	*Solvothermal synthesis of doped hematite/reduced graphene oxide nanocomposites for sodium-ion batteries*

16.20 - 16.30	**IND OR038**	**Emilia Paone**	*Reductive Upgrading of Biomass Derived Furan promoted by Spent Lithium-Cobalt Batteries as an Efficient Heterogeneous Catalyst*
16.30 - 16.40	**IND OR039**	**Matteo Bonomo**	*Thermosetting polyurethanes resins: application as cheap, sustainable and scalable encapsulants for (flexible) Perovskite Solar Cells*
16.40 - 16.55	***Discussion***		
16.55 - 17.10	**break**		
17.10 - 17.20	**IND OR040**	**Andrea Fasolini**	*Low Temperature Methane Steam Reforming in a H2-selective Pd Membrane Reactor*
17.20 - 17.30	**IND OR041**	**Tiziano Montini**	*Visible-light-driven coproduction of diesel precursors and hydrogen from lignocellulose-derived methylfurans*
17.30 - 17.40	**IND OR042**	**Nicola Sangiorgi**	*Improved water stability of CsPbBr3 thin film photoelectrodes*
17.40 - 17.50	**IND OR043**	**Cosimo Micheletti**	*Luminescent Solar concentrators based on Aggregation-Induced Emission*
17.50 - 18.00	**IND OR022**	**Giuseppe Pipitone**	*Aqueous phase reforming of biorefinery by-products towards sustainable hydrogen production*
18.00 - 18.10	**IND OR045**	**Francesco Conte**	*H2 production by photoreforming of glucose*
18.10 - 18.30	***Discussion***		

Divisione CHIMICA ORGANICA (ORG)
ORG 08

15.00 - 15.30	**ORG PZ006**	**Daniela Montesarchio**	***Premio alla ricerca Chimica Organica per le Scienze della Vita*** *G-Quadruplexes to the fore: towards DNA-targeting magic bullets*
15.30 - 16.00	**Break**		
16.00 - 16.15	**ORG PZ014**	**Anna Esposito**	***Premio Tesi di Dottorato Chimica Organica per le Scienze della Vita*** *Exploring the therapeutic potential of L-deoxyiminosugars in rare diseases*
16.15 - 16.30	**ORG OR045**	**Cristina Minnelli**	*Epigallocatechin-3-gallate-based Inhibitors Targeting EGFR to Overcome Drug Resistance in Advanced NSCLC*
16.30 - 16.45	**ORG OR046**	**Lucía Morillas Becerril**	*Specific and nondisruptive interaction of guanidium-functionalized gold nanoparticles with neutral phospholipid bilayers*
16.45 - 17.00	**ORG OR047**	**Maria Luisa Navacchia**	*Dihydroartemisinin-bile acid hybridization as an effective approach to enhance dihydroartemisinin anticancer activity*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR048**	**Ferran Nieto Fabregat**	*Gram-negative bacteria LPS recognition by DC-SIGN*

17.45 - 18.00	**ORG OR049**	**Anna Notaro**	*Mimiviruses possess the biosynthetic pathways to produce bacteria-like sugars in a clade-specific manner*
18.00 - 18.15	**ORG OR050**	**Alessandro Palmioli**	*On-cell saturation transfer difference NMR for the identification of FimH ligands and inhibitors*
18.15 - 18.30	**ORG OR051**	**Daniela Perrone**	*Synthesis and preclinical evaluation of antisense oligonucleotides conjugated with ursodeoxycholic acid for the treatment of Duchenne muscular dystrophy*

ORG 09

16.00 - 16.15	**ORG PZ013**	**Mirko Maturi**	***Premio Tesi di Dottorato Chimica Organica per l'Ambiente, l'Energia e le Nanoscienze*** *Advanced Functional Organic-Inorganic Hybrid (Nano)Materials: from Theranostics to Organic Electronics and Additive Manufacturing*
16.15 - 16.30	**ORG OR052**	**Mariacecilia Pasini**	*Sustainable by Design Carbon Dots as promising material for luminescent and biomedical applications*
16.30 - 16.45	**ORG OR053**	**Vincenzo Patamia**	*A new hybrid porous multifunctional material based on Loofah-Halloysite*
16.45 - 17.00	**ORG OR054**	**Marina Massaro**	*Synthesis and characterization of different mussel inspired materials for several applications*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR055**	**Giulia Neri**	*Fluorinated Polymers and Fluorescent Graphene as Innovative Nanotheranostic Materials*
17.45 - 18.00	**ORG OR056**	**Alessandra Operamolla**	*Cellulose nanocrystals for paper consolidation*
18.00 - 18.15	**ORG OR057**	**Luca Pettazzoni**	*Transamidation-based vitrimers from renewable sources*
18.15 - 18.30	**ORG OR058**	**Serena Riela**	*Improvement of properties of halloysite and some other «friends» by chemical modifications*

ORG 10

16.00 - 16.15	**ORG OR059**	**Claudio Curti**	*Merging Vinylogy with Organocatalysis: Direct, Asymmetric Entry to Chiral Fused Uracil Derivatives*
16.15 - 16.30	**ORG OR060**	**Daniele Fiorito**	*Synthetic studies towards Bastimolide B*
16.30 - 16.45	**ORG OR061**	**Paola Costanzo**	*Highly oleophilic and reusable polyurethane composites for the removal of oils from fresh water and seawater*
16.45 - 17.00	**ORG OR062**	**Andrea Mezzetta**	*Reactive Deep Eutectic Solvents (ReDESs): an underexploited option for organic chemistry*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR063**	**Lorenzo Di Terlizzi**	*Visible light-driven α-arylation of enol silyl ethers via arylazo sulfones.*

17 settembre - pomeriggio

17.45 - 18.00	**ORG OR064**	**Lucia Ferrazzano**	*Greening peptide synthesis: new options for a sustainable chemistry*
18.00 - 18.15	**ORG OR065**	**Valeria Nori**	*Organocatalysed Michael addition of masked acetaldehyde to nitroalkenes in water*
18.15 - 18.30	**ORG OR066**	**Rita Mocci**	*Mechanochemical Fischer Indolisation: Exploration of a Timeless Reaction in a New Guise*

ORG 11

16.00 - 16.15	**ORG OR067**	**Allegra Franchino**	*Merging organo- and Au(I) catalysis for asymmetric or silver-free reactions of alkynes*
16.15 - 16.30	**ORG OR068**	**Gianluigi Albano**	*Infrared irradiation-assisted solvent-free Palladium-catalyzed (hetero)aryl-aryl coupling via C-H bond activation*
16.30 - 16.45	**ORG OR069**	**Fabio Bellina**	*Pd/Ag-mediated dehydrogenative alkynylation of imidazoles*
16.45 - 17.00	**ORG OR070**	**Silvia Gaspa**	*Photocatalyzed amides synthesis from alcohols by visible light*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR071**	**Fabrizio Medici**	*Stereoseletive [2+2] photocycloaddition: a viable strategy for the synthesis of enantiopure cyclobutane derivatives*
17.45 - 18.00	**ORG OR072**	**Francesco Messa**	*Ligand-Free Cobalt-Catalyzed Cross-Coupling Reaction Between Organoaluminum Reagents and (Hetero)Aryl and Alkyl Bromides*
18.00 - 18.15	**ORG OR073**	**Giorgia Zanchin**	*Imino-pyridine Cr complexes as precatalyst for the polymerization of olefins: synthesis and catalytic tests with NEt3 as additive*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 03

15.00 - 15.30	**CSB KN003**	**Luc Brunsveld**	*Stabilization of Protein-Protein Interactions; from the fundamentals of cooperativity to applications in drug discovery*
15.30 - 15.45	**CSB OR014**	**Alessio Romerio**	*Design, synthesis and Biological evaluation of New, glycolipid-based Toll-Like Receptor 4 (TLR4) Modulators*
15.45 - 16.00	**CSB OR015**	**Giusy Tassone**	*Evidence of amino-thiadiazoles as innovative inhibitors of human glutaminyl cyclase, validated target for neurodegenerative disorders*
16.00 - 16.15	**CSB OR016**	**Francesco Tadini-Buonisegni**	*Modulation of Ca2+-ATPase transport activity by pharmacologically relevant compounds*
16.15 - 16.30	**CSB OR017**	**Michela Pisani**	*Insulin loaded in liquid crystalline mesophases: effects on carrier structure and insulin stability*
16.30 - 17.00	**Break**		

17.00 - 17.30	**CSB KN004**	**Elena Sgaravatti**	*Research and development of active ingredients from vegetable cells or crops to be used in the Health care, Food and Personal care sectors*
17.30 - 17.45	**CSB OR018**	**Valeria Romanucci**	*New curcumin mimics based on tyrosol scaffold: investigation of neuroprotective and anticancer activity*
17.45 - 18.00	**CSB OR019**	**Roberto Tira**	*Modulation of Tau aggregation with natural coffee compounds*
18.00 - 18.10	**CSB OR020**	**Rita Pagano**	*Phosphate-linked Silybin dimers: synthesis and investigation of biological activity*
18.10 - 18.20	**CSB OR021**	**Massimiliano Gaeta**	*Hybrid Porphyrin/DOPA-melanin Film as Versatile Biomaterial for Water Remediation*
18.20 - 18.50	**Discussione**		

Divisione DIDATTICA CHIMICA (DID)
DID 02

15:00-15:30	**DID IL002**	**Carlo Fiorentini**	*The teaching of chemistry from the perspective of citizenship*
15:30-15:45	**DID OR010**	**Teresa Cecchi**	*Chemistry: a Precious Discovery in the Dantesque World*
15:45-16:00	**DID OR011**	**Maria Irene Donnoli**	*A Carbon atom journey*
16:00-16:15	**DID OR012**	**Elena Lenci**	*Peer review of scientific articles: a teaching experience*
16:15-16:30	**DID OR013**	**Silvia Prati**	*Increasing the engagement of non-chemistry major students: examples of didactic strategic*
16:30-18:30	**Panel Discussion**	**Silvia Bencivelli (coordinator)** **Pellegrino Conte** **Paola Govoni** **Piersandro Pallavicini** **Valentina Domenici**	*Chemistry: how, where, when and why*

Divisione SPETTROMETRIA DI MASSA (MAS)
MAS 02

15.00 - 15.40	**MAS PL003**	**Nikolai Kuhnert**	*Mass spectrometry in coffee science: From bean to drink to human*
15.40 - 16.10	**MAS KN001**	**Tata Alessandra**	*Non-targeted authentication of food products: the synergic combination of ambient mass spectrometry, data fusion and machine learning"*
16.10 - 16.25	**MAS OR006**	**M.A. Acquavia**	*Influence of mixed starter cultures of Hanseniaspora osmophila and Saccharomyces cerevisiae on wine flavor profile explored through HS-SPME/GC-MS*
16.25 - 16.35	**Break**		

16.35 - 17.05	**MAS KN002**	**Linda Monaci**	*Future challenges in MS based technologies applied to the safety of foods.*
17.05 - 17.20	**MAS OR007**	**Rosalia Zianni**	*Lipidomic approach to evaluate the effect of X-ray irradiation treatment on the lipid profile of Camembert cheese*
17.20 - 17.35	**MAS OR008**	**Fabiola De Marchi**	*High-resolution mass spectrometry approaches finalized to identification of new glycoside compounds in grape*
17.35 - 17.50	**MAS OR009**	**Ciro Cannavacciuolo**	*Analysis by high-resolution mass spectrometry of polyphenolic alkaloids fraction from Portulaca oleracea*
17.50 - 18.05	**MAS OR010**	**Lucia Bartella**	*Paper Spray tandem mass spectrometry: an innovative approach to assess flavonoid content in citrus drinks*

Divisione TEORICA E COMPUTAZIONALE (TEO)

TEO 02

15.00 - 15.30	**TEO KN002**	**Alfonso Pedone**	*Exploiting Machine Learning Methods in Atomistic Simulations of Oxide Glasses*
15.30 - 15.45	**FIS OR059**	**Adriana Pecoraro**	*First-principles study of Mn and Fe co-doped BaZrO3 as PC-SOFC cathode for the Oxygen Reduction Reaction*
15.45 - 16.00	**TEO OR013**	**Leonardo Guidoni**	*Quantum Chemistry using Quantum Computers*
16.00 - 16.15	**FIS OR061**	**Marco Medves**	*TDDFT methods for large systems: new computational schemes and automatic generation of density fitting basis*
16.15 - 16.30	**TEO OR014**	**Elena Tocci**	*Molecular view on crystals nucleation and growth on different PVDF polymorphs*
16:30 - 17:00	**Discussion**		

TEO 03

15:00 - 15:10	**TEO OR015**	**Matteo Capone**	*Multi-Scale Charge-Transfer Modeling in Enzyme Catalysis*
15:10 - 15:20	**TEO OR016**	**Guelber Cardoso Gomes**	*Computational study of dicationic ionic liquids based on imidazole*
15:20 - 15:30	**TEO OR017**	**Elisa Bernes**	*An experimental and theoretical investigation on the electronic structure of indole, 2,3-dihydro-7- azaindole, and 3-formylindole in the gas phase by synchrotron-based spectroscopic techniques*
15:30 - 15:40	**TEO OR018**	**Yasi Dai**	*Addressing the Frenkel and charge transfer character of exciton states with a model Hamiltonian based on dimer calculations: application to large aggregates of perylene bisimide*

17 settembre - pomeriggio

15:40 - 15:50	**TEO OR019**	**Stefano Motta**	*Study of ligand binding to HIF-2α through Path-Metadynamics*
15:50 - 16:00	**TEO OR020**	**Alessandra Gilda Ritacca**	*The multifaceted roles of copper ion in human body explored by computational tools*
16:00 - 16:10	**TEO OR021**	**Anna Rovaletti**	*Unravelling the reaction mechanism of Mo/Cu CO dehydrogenase using QM/MM calculations*
16:10 - 16:20	**TEO OR022**	**Sara Del Galdo**	*How water density responds to the presence of a crowding agent*
16:20 - 16:30	**TEO OR023**	**Francesco Ferdinando Summa**	*SYSMOIC: A Program Package for the Calculation of Origin-Independent Electron Current Density and Derived Magnetic Properties in Molecular Systems*
16:30 - 17:00	**break**		
17:00 - 17:20	**TEO KN003**	**Fabrizia Negri**	*Modelling extended-core π systems and their aggregates: charge transport and optoelectronic properties*
17:20 - 17:40	**TEO PZ003**	**Giovanni Di Liberto**	*Rational Design of Semiconductor Interfaces for Photocatalysis*
17:40 - 18:00	**TEO PZ004**	**Eduardo Schiavo**	*First Principles Approaches for Heterogeneous Functional Materials*
18:00 - 18:30	**Discussion**		

Programma dei LAVORI di DIVISIONE - 20 settembre mattina

Divisione CHIMICA ORGANICA (ORG)

ORG 12

9.30 - 10.00	**ORG PZ004**	**Pierangelo Gobbo**	***Medaglia Giacomo Ciamician*** *A synthetic chemistry approach to the fabrication of protocells and protocellular materials*
10.00 - 10.30	**ORG PZ007**	**Francesco Giacalone**	***Premio alla ricerca Chimica Organica per l’Ambiente, l’Energia e le Nanoscienze*** *Nanocarbon-based Hybrid Materials as Efficient and Sustainable Heterogeneous Catalysts*
10.30 - 10.45	**ORG OR074**	**Loredana Maiuolo**	*Polysubstituted 1,2,3-Triazoles: synthesis and biological application*
10.45 - 11.00	**ORG OR075**	**Michele Mancinelli**	*Atropisomeric Azaborines: Axial Chirality at the Boron-Carbon Bond*
11.00 - 11.15	**ORG OR076**	**Francesca Franco**	*Formal α-trifluoromethylthiolation of carboxylic acid derivatives via N-acyl pyrazoles*
11.15 - 11.30	**ORG OR077**	**Claudia Sciacca**	*Synthesis of nitrogenated analogues of honokiol as potential bioactive compounds*
11.30 - 11.45	**ORG OR078**	**Damiano Tanini**	*The unexpected role of Se(IV) vs Se(VI) species in the on water selenium-catalysed oxidation of anilines*
11.45 - 12.00	**ORG OR079**	**Claudio Zippilli**	*Double strategies for regioselective one-pot C-H oxidative functionalization of coumarins*

ORG 13

10.30 - 10.45	**ORG OR080**	**Chiara Liliana Boldrini**	*Eco-friendly deep eutectic solvent electrolyte solutions for dye-sensitized solar cells*
10.45 - 11.00	**ORG OR081**	**Gabriella Buscemi**	*Polydopamine/ethylenediamine nanoparticles embedding a bacterial photoenzyme for solar energy conversion*
11.00 - 11.15	**ORG OR082**	**Mattia Forchetta**	*Design of KuQuinone-Co3O4 nanoparticle hybrid dyads for photoelectrochemical applications*
11.15 - 11.30	**ORG OR083**	**Giulio Goti**	*Fluorescent Materials for the Enhancement of the Photosynthetic Efficiency*
11.30 - 11.45	**ORG OR084**	**Norberto Manfredi**	*Photo(electro)catalytic water splitting using Calix[4]arene-Based dyes*
11.45 - 12.00	**ORG OR085**	**Lorenzo Zani**	*Construction of tailored, donor-acceptor heterocyclic compounds for solar energy conversion*

ORG 14

10.30 - 10.45	**ORG OR086**	**Achille Antenucci**	*How do arenediazonium salts behave in Deep Eutectic Solvents? A combined experimental and computational approach*
10.45 - 11.00	**ORG OR087**	**Laura Baldini**	*Halogen-bonded architectures of multivalent calix[4]arenes*
11.00 - 11.15	**ORG OR088**	**Daniele Del Giudice**	*pH Transient Variation Triggered by Nitroacetic Acid Allowing Dissipative Control in Supramolecular Systems*
11.15 - 11.30	**ORG OR089**	**Oscar Francesconi**	*A tweezers-shaped receptor for the biomimetic recognition of the GlcNAc2 disaccharide in water*
11.30 - 11.45	**ORG OR090**	**Giorgio Olivo**	*Supramolecular Remote C(sp3)-H Oxidation*
11.45 - 12.00	**ORG OR091**	**Daniele Rosa-Gastaldo**	*Tuning the folding properties of synthetic recognition-encoded oligomers*

Programma dei LAVORI di DIVISIONE - 21 settembre mattina

Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

ABC 05

09.30-09.45	**Presentation**		
09.45-10.00	**ABC OR046**	**P. Guzmán García Lascurain**	*Agar foam for the cleaning of art surfaces: a new approach*
10.00-10.15	**FIS OR 129**	**David Chelazzi**	*pHEMA/PAA and pHEMA/PVP semi-IPNs: physico-chemical characterization and use for bronze cleaning*
10.15-10.30	**FIS OR128**	**Francesco Armetta**	*Unusual corrosion of bronze helmets discovered in Mediterranean seabed*
10.30-10.45	**ABC OR047**	**Francesca Ramacciotti**	*Advanced systems for the cleaning of Cultural Heritage*
10.45-11.00	**FIS OR 127**	**Leonardo Severini**	*Ultrasound-stimulated PVA microbubbles as removal tool for adhesive tapes from cellulose-based materials*
11.00-11.15	**ABC OR048**	**Elisabetta Zendri**	*Evaluation of a new setup to improve the electro-kinetic desalination of porous materials in Cultural Heritage*
11.15-11.30	**break**		
11.30-11.45			
11.45-12.00	**ABC OR049**	**Marco Valente Chavez Lozano**	*Deep Eutectic Solvents (DES) based on choline chloride and betaine for cleaning gelatin residues from cellulose nitrate cinematographic films.*
12.00-12.15	**ABC OR050**	**Giuseppe Lazzara**	*Halloysite nanotubes: a versatile material for conservation of cultural heritage*
12.15-12.30	**ABC OR012**	**Francesca Nardelli**	*Insights into the oil paint polymeric network by Solid State NMR*
12.30-12.45	**ABC OR031**	**Carolina Rigon**	*Discovering the Maya ritual practices through the study of pigmented human bones remains by Archaeometry investigation*
12.45-13.00		**Antonio Marcomini**	*Conclusioni*

ABC 06

09.30-09.50	**ABC KN002**	**Fabrizio Passarini**	*The tool of LCA to analyse and improve the sustainability of chemical processes*
09.50-10.00	**IND OR046**	**Prisco Prete**	*New biodegradable catalysts for photo-Fenton like process for wastewater treatment reuse in a circular economy perspective*

10.00-10.10	**ABC OR053**	**Damiano Sgherza**	*Integrating biodegradation and ozone-catalysed oxidation for treatment of biomass gasification wastewater*
10.10-10.20	**IND OR047**	**Stefano Andrea Balsamo**	*One-pot synthesis of TiO2-rGO photocatalysts for the degradation of groundwater pollutants*
10.20-10.30	**ABC OR054**	**Luisa Barbieri**	*An integrated system for a new controlled release fertilizer based on lightweight ceramic aggregates starting from waste materials and bio-products*
10.30-10.40	**IND OR048**	**Ermelinda Falletta**	*Efficient day-and-night NO2 abatement by polyaniline/TiO2 composites*
10.40-10.50	**ABC OR055**	**Pietro Calandra**	*Reutilization of residues from municipal wastes pyrolysis to improve and regenerate asphalts*
10.50-11.00	**Discussion**		

Modellazione ambientale e caratterizzazione chimica degli aerosol atmosferici/Environmental

11.15-11.30	**ABC OR056**	**Loris Calgaro**	*Exposure modelling of emerging contaminants in the Venice lagoon - a case-study on active pharmaceutical ingredients*
11.30-11.45	**ABC OR057**	**Federtica Zennaro**	*Modelling eutrophication processes in the Venice Lagoon: a multivariate Machine Learning approach*
11.45-12.00	**ABC OR058**	**Pierluigi Barbieri**	*Bioaerosol detection, pathogen airborne transmission and abatement studies: capacity building, experimental results and perspectives from the COVID-19 pandemic*
12.00-12.15	**ABC OR059**	**Manuel Amedeo Cefali**	*Evaluation of PMx chemical composition and planning of a vegetable-green barrier in a high traffic site in Milan*
12.15-12.30	**ABC OR060**	**Niccolo Losi**	*Aerosol characterization from the tropics to the North Pole*
12.30-12.45	**ABC OR061**	**Alessandro Mancini**	*X-Ray Diffraction of Non-Exhaust Emissions generated from Braking: How to Assess the Phase Composition of the Crystalline Fraction*
12.45-13.00		**Antonio Marcomini**	*Conclusioni*

Divisione CHIMICA FARMACEUTICA (FAR)

FAR 07

09.30 - 10.00	**FAR KN009**	**Anders Bach**	*Targeting protein-protein interactions involved in oxidative stress using fragment-based drug discovery*

21 settembre - mattina

10.00 - 10.30	**FAR KN010**	**Giancarlo Aldini**	*Chemical and molecular mechanisms of cellular and extra-cellular antioxidants*
10.30 - 10.45	**FAR OR031**	**Marco Catto**	*A second life for MAO inhibitors: from CNS diseases to cancer*
10.45 - 11.00	**FAR OR032**	**Stefano Sainas**	*Apoptotic and differentiating therapy for AML using potent human dihydroorotate dehydrogenase inhibitor*
11.00 - 11.30	**FAR KN011**	**Tiziano Bandiera**	*Discovery of a picomolar potency corrector of F508del-CFTR chloride channel*
11.30 - 11.45	**FAR OR035**	**Francesca Spyrakis**	*Identification of carbapenemase broad-spectrum inhibitors through in silico methodologies*
11.45 - 12.00	**FAR OR036**	**Serena Massari**	*1,2,4-Triazolo[1,5-a]pyrimidines: efficient one-step synthesis and functionalization as antiviral agents*
12.00 -12.15	**FAR OR037**	**Alessandra Altomare**	*An integrated metabolomic and proteomic approach for the identification of covalent inhibitors of the main protease (Mpro) of SARS- COV-2 from crude natural extracts*
12.15 -12.30	**FAR OR038**	**Antonella Messore**	*Discovery of non-DKA derivatives endowed of selective activity against ribonuclease H function of the HIV-1 reverse transcriptase*
12.30 - 13.00	**FAR KN012**	**Pedro Gois**	*Exploring B-complexes as likers for targeting drug conjugates*

FAR 08

10.30 - 10.45	**FAR OR033**	**Claudia Sorbi**	*Constrained 1,4-dialkylpiperazines as dopamine transporter (DAT) inhibitors to fight psychosis and cocaine addiction*
10.45 - 11.00	**FAR OR034**	**Elisa Uliassi**	*Psychotropic-based bifunctional compounds for neurodegenerative diseases*
11.00 - 11.30			
11.30 - 11.45	**FAR OR039**	**Salvatore Di Maro**	*Peptides from bench to clinical studies: our experience with CXCR4*
11.45 - 12.00	**FAR OR040**	**Azzurra Stefanucci**	*A novel β-hairpin peptide derived from the ARC repressor selectively interacts with the major groove of B-DNA*
12.00 -12.15	**FAR OR041**	**Stefano Tomassi**	*Shading the activity of a CXCR4-interacting peptide by 1,4- and 1,5-disubstituted [1,2,3]-triazole-based cyclization*

12.15 -12.30	**FAR OR042**	**Rosa Bellavita**	*Grafting Temporin L peptides: old tactics for new antimicrobial weapons*

Divisione CHIMICA FISICA (FIS)

FIS 08

Cultural Heritage and Environment

09:30-10:00	**FIS KN010**	**Gabriella Di Carlo**	*Corrosion protection in Concrete Heritage: from material design to in situ validation*
10:00-10:15	**FIS OR072**	**Lorenzo Lisuzzo**	*Pickering Emulsions Based on Wax and Halloysite Nanotubes for the Treatment of Archeological Woods*
10:15-10.30	**FIS OR073**	**Vanessa Rosciardi**	*Biocomposite Poly(Vinyl Alcohol)/Starch cryogels: green tailorable tools for the cleaning of painted artworks*
10:30-10.45	**FIS OR074**	**Rosangela Mastrangelo**	*Cleaning Pollock's and Picasso's masterpieces: the physical chemistry behind the scenes*
10:45-11:00	**FIS OR075**	**Giovanna Poggi**	*Adaptive castor-oil based organogels: synthesis, characterization and use for the selective and controlled cleaning of works of art*
11:00-11.15	**FIS OR076**	**Michele Baglioni**	*Nanostructured Fluids For Polymeric Coatings Removal: Surfactants Affect the Polymer Glass Transition Temperature*
11:15-11.30	**FIS OR077**	**Sara Morandi**	*Pd-promoted zeolites for low-temperature NOx adsorption*
11.30-11.45	**break**		

Physical Chemistry of Sensors

11:45-12:00	**FIS OR078**	**Lucio Litti**	*Surface Enhanced Raman Scattering toward applications*
12:00_12:15	**FIS OR079**	**Stefano Toffanin**	*Organic optoelectronic components in highly integrated systems for plasmonics sensing in food security/quality*
12:15-12.30	**FIS OR080**	**Simona Bettini**	*SERS-SPR COUPLING FOR ULTRASENSITIVE DETECTION OF DOPAMINE IN ARTIFICIAL CEREBROSPINAL FLUID.*
12:30-12:45	**FIS OR081**	**Cristina Chirizzi**	*A bimodal imaging probe for combined Raman microscopy and 19F-MRI*
12:45-13:00	**FIS OR082**	**Giovanni De Filpo**	*Novel pressure sensors based on elastomeric PDLC films*
13:00-13:15	**FIS OR083**	**Francesco Tavani**	*Investigating the interfacial solvation properties of the Mg2+ ion by operando soft X-ray absorption spectroscopy at ambient pressure and simulations*

FIS 09

Physical Chemistry of Materials I

09:30-10:00	**FIS KN011**	**Luciano Galantini**	*From Molecules to Supracolloidal Atomium like Superstructures: Building from the Bottom-Up with Steroidal Amphiphiles*
10:00-10:15	**FIS OR084**	**Mario Prosa**	*Organic light-emitting transistors: advanced materials and innovative architectures towards a real-setting application*
10:15-10.30	**FIS OR085**	**Pietro Calandra**	*Mixing liquid amphiphiles to prepare organic fluids fully responsive to a magnetic field*
10:30-10.45	**FIS OR086**	**Valerio Loianno**	*A Hyphenated Approach Combining Pressure-Decay and In Situ FT-NIR Spectroscopy to Monitor Penetrant Sorption and Concurrent Swelling in Polymers*
10:45-11:00	**FIS OR087**	**Maria Rosaria Plutino**	*Design and development of multifunctional hybrid surface coatings for advanced and smart applications on textiles*
11:00-11.15	**FIS OR088**	**Federico Begni**	*Hyper Cross - Linked Polymers as additives for preventing aging of PIM1 membranes*
11:15-11.30	**FIS OR089**	**Chiara Nomellini**	*WO3-BiVO4 heterojunction: effects of WO3 nanostructuring on the photoelectrochemical performance*

Physical Chemistry of Materials II

11:45-12:00	**FIS OR090**	**Alberto Girlando**	*Charge-Transfer Soft Ferroelectrics*
12:00_12:15	**FIS OR091**	**Marco Sanna Angotzi**	*Designing Spinel Ferrite-Based Nano-Heterostructures Through Versatile Solvothermal Approaches*
12:15-12.30	**FIS OR092**	**Stefano Alberti**	*Physico-Chemical Characterization of Polydimethylsiloxane Electrospun Fibers*
12:15-12.30	**FIS OR051**	**Alessandro Piovano**	*A deep description of the electronic properties of Ti sites in Ziegler-Natta catalysts from advanced spectroscopic methods*
12:45-13:00	**FIS OR094**	**Matteo Busato**	*Structural Characterization of Deep Eutectic Solvents Mixtures with Water and Methanol*
13:00-13:15	**FIS OR095**	**Michele Porto**	*Use of REOBs and industrial by-products additives for new bitumen-like material formulation: chemical physical and mechanical characterization*

Divisione CHIMICA INORGANICA (INO)

INO 07

9.30 - 10.50	**INO PZ006 (Premio Dottorato 2021)**	**Fabio Pirro**	*De novo design of multi-domain metalloenzymes*
9.50 - 10.10	**INO PZ007 (Premio Dottorato 2021)**	**Matteo Vanni**	*Reactivity of Black Phosphorus with Pd Compounds*
10.10 - 10.30	**INO PZ008 (Premio Dottorato 2021)**	**Alessandra Barbanente**	*Targeted Delivery of Anticancer Platinum Complexes to Bone Tumors and Metastases “non classical” compounds mechanism of action*
10.30 - 10.45	**INO OR043**	**Rita Mazzoni**	*Cyclopentadienone-NHC Iron(0) electrocatalysts for water oxidation*
10.45 - 11.00	**INO OR044**	**Anna Pintus**	*Ammonium salts of oxalic acid derivatives: a new family of agents for the conservation of carbonate stone substrates of artistic value*
11.00 - 11.15	**INO OR045**	**Andrea Fermi**	*Visible-light activated metallaphotoredox catalysis enabled by TiIV complexes: new routes for C-C bond formation*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR046**	**Riccardo Pedrazzani**	*Correlating solid-state analysis and catalysis: exploring secondary π-interactions effects in Au(I) catalyzed reactions*
11.45 - 12.00	**INO OR047**	**Rossana Galassi**	*When metallaphilia makes the difference: the case of stacked coinage metals Trinuclear Cyclic Compounds*
12.00 - 12.15	**INO OR048**	**Alessia Belloni**	*FTIR-HSI analysis of triple-negative breast cancer (TNBC)*
12.15 - 12.30	**INO OR049**	**Francesca Gambassi**	*A Cu(II)-MOF based on a propargyl carbamate-functionalized isophthalate ligand*
12.30 - 13.00	**INO IL002**	**Anke Weidenkaff**	*Circular Materials for the Energy Transition*

INO 08

10.30 - 10.45	**INO OR050-ad hoc**	**Marzio Rancan**	*Hierarchical chiral transfer in bright lanthanides quadruple stranded helicate-cages by host-guest interaction*
10.45 - 11.00	**INO OR051**	**Giuseppe Ferrauto**	*Hydrophobic interactions between macrocyclic Gd-complexes and polyaromatic systems as route to enhance the longitudinal water relaxivity in Magnetic Resonance Imaging*

11.00 - 11.15	**INO OR052**	**Salvatore Impemba**	*Dinuclear Thioether-amide Aluminum Complexes in the Ring Opening Polymerization of Cyclic Esters*
11.15-11-30	**break**		
11.30 - 11.45	**INO OR053**	**Paolo Pelagatti**	*Put light on inside a microporous MOF to decipher the guest arrangement and guest- release properties*
11.45 - 12.00	**INO OR054**	**Francesca Garello**	*Biodegradable polyelectrolyte/magnetite capsules for MR imaging and magnetic targeting of tumors*
12.00 - 12.15	**INO OR055**	**Letizia Liccardo**	*CeOx/TiO2 Hollow Spheres as efficient photocatalyst for the degradation of organic pollutants in wastewater*
12.15 - 12.30	**INO OR056**	**Denise Lovison**	*Highly active ruthenium complexes: synthesis and evaluation of the anticancer activity through interaction with relevant biomolecules*

INO 09

10.30 - 10.45	**INO OR057**	**Gabriele Manca**	*Reactivity of imidazolate Au(I) cyclictrinuclearcompounds, CTCs, with iodine or MeI: a computational/experimental study*
10.45 - 11.00	**INO OR058**	**Luca Andreo**	*DFT and semi-empirical GFN2-xTB methods: experimental and computational characterization of an Iron(II) carbene complex*
11.00 - 11.15	**INO OR059**	**Mario Prejanò**	*How lanthanide ions affect the catalytic activity of methanol dehydrogenase: a computational point of view*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR060- ad hoc**	**Daniela Marasco**	*Transition metal complexes as neurodrugs: insights into their modulation of amyloid aggregation*
11.45 - 12.00	**INO OR061**	**Laura Del Coco**	*X. fastidiosa affecting olive trees in Salento: metal ions in soil, plants and treatment compounds*
12.00 - 12.15	**INO OR062**	**Antonino Famulari**	*Unveiling electronic and structural properties of, peroxygenase-like cytochrome P450, CYP116B5hd*
12.15 - 12.30	**INO OR063**	**Davide Corinti**	*Elusive intermediates in the reactivity of platinum(IV) prodrugs: a new perspective on their bioactivation*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)

TEC 05

09.30 - 10.00	**TEC IL003**	**Alessandro Gori**	*Liquid biopsy at the crossroads of chemistry and technology: the extracellular vesicles case study*

21 settembre - mattina

10.00 - 10.15	**TEC KN003**	**Serena De Santis**	*Fourier transform IR micro-spectroscopy of biological tissues: a promising tool for diagnostic and assessment of tissue functionality.*
10.15 - 10.30	**TEC KN004**	**Andrea Melchior**	*Diclofenac adsorption on carbon-based nanomaterials: a molecular dynamics study*
10.30 - 10.40	**TEC OR041**	**Francesca Baldassarre**	*Utilization of biosourced materials in chemical nanotechnologies developing controlled release systems for human and plants health*
10.40 - 10.50	**TEC OR042**	**Paola Astolfi**	*Structural characterization and in-vitro anticancer activity of nanovectors for delivery of bioactive coumpounds*
10.50 - 11.00	**TEC OR043**	**Arianna Rossetti**	*3D integration of pH-cleavable drug-hydrogel conjugates on magnetically driven smart microtransporters*
11.00 - 11.10	**TEC OR044**	**Falcone Giovanni**	*Calcium Alginate hydrogels in Semi Solid Extrusion 3D printing: physico-chemical requirements for high printing performance*
11.10 - 11.30	**Discussion**		
11.30 - 11.40	**TEC OR045**	**Anita Ceccucci**	*Mixed oxide Cerium coating for improved titanium nanotubes bioactivity*
11.40 - 11.50	**TEC OR046**	**Clelia Dispenza**	*Adipose stem cell spheroids-laden hydrogels for minimally invasive bone and cartilage regeneration interventions*
11.50 - 12.00	**TEC OR047**	**Emanuela Muscolino**	*k- Carrageenan and PVA blends as bioinks to 3D print scaffolds for cartilage reconstruction*
12.00 - 12.10	**TEC OR048**	**Edoardo Testa**	*Adducts of functionalized graphene layers with Ag nanoparticles for antimicrobial applications*
12.10 - 12.30	**Discussion**		
12.30 - 12.50	**break**		
12.50 - 13.00	**TEC OR049**	**Martina Sanadar**	*A novel luminescent Europium(III) complexes for citrate detection*
13.00 - 13.10	**TEC OR050**	**Gaspare Varvaro**	*Co/Pd-based synthetic antiferromagnetic multi-stacks for biomedical applications*
13.10 - 13.20	**TEC OR051**	**Alessandra Vitale**	*Coupling electrospinning and photo-induced crosslinking to produce shape-stable rubber nanofibrous membranes*
13.20 - 13.30	**TEC OR052**	**Antonino Rizzuti**	*Analysis of the chemical profile of sparkling wines fermented with autochthonous yeast strains using a non-targeted metabolomic approach*
13.30 - 13.50	**Discussion**		

13.50 - 14.00	**CONCLUSIONE**

Divisione ELETTROCHIMICA (ELE)

ELE 08

09.30 - 10.00	**ELE_IL50**	**Piotr Zelenay**	*Oxygen Reduction at Platinum Group Metal-Free Fuel Cell Catalysts:Piotr Recent Progress*
10.00 - 10.15	**ELE_OR51**	**Alessandro Facchin**	*From Redox-like to Heterogeneous Electrocatalysis at Metal-Octaethylporphyrins@HOPG investigated by EC-STM*
10.15 - 10.30	**ELE_OR52**	**Lucia Mazzapioda**	*Non-stoichiometric Metal Oxide Particles as Active Electrode Component in PEM Fuel Cells*
10.30 - 10.45	**ELE_OR53**	**Simone Bonizzoni**	*Aquivion®-based Alkaline Membrane for Fuel Cell and Electrolyzer Applications*
10.45 - 11.00	**ELE_OR54**	**Antunes Staffolani**	*Identification of Solid Oxide Cells Processes by Distribution of Relaxation Times: Model Creation and Validation*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE_KN55**	**Lior Elbaz**	*Design of Aerogel-based Electrocatalysts for ORR*
11.45 - 12.00	**ELE_OR56**	**Davide Cademartori**	*Anode-supporting substrates with hierarchical porosity manufactured with freeze tape casting for reversible solid oxide cells*
12.00 - 12.15	**ELE_OR57**	**Vincenzo Baglio**	*Electrospun MnCo2O4/CNF as Oxygen Electrode for Alkaline Zn-Air Batteries*
12.15 - 12.30	**ELE_OR58**	**Eleonora Pargoletti**	*Disclosing the Electrocatalytic Behavior of Doped-MnO2 for Lithium-Air Batteries*

ELE 09

09.30 - 10.00	**ELE_IN59**	**Doron Auerbach**	
10.00 - 10.15	**ELE_OR60**	**Keti Vezzù**	*Innovative Olivine Cathodes for High-Voltage Lithium Batteries*
10.15 - 10.30	**ELE_OR61**	**Akiko Tsurumaki**	*Highly Versatile Gel Polymer Electrolytes for High Voltage Lithium Batteries*
10.30 - 10.45	**ELE_OR62**	**Marisa Falco**	*Protic ionic liquid electrolytes in lithium metal cells*
10.45 - 11.00	**ELE_OR63**	**Lorenzo Mezzomo**	*Long life lithium metal batteries employing dendrite-eating nanocomposite solid-state electrolytes based on hybrid fillers.*
11.00 - 11.15	**break**		

11.15 - 11.45	**ELE_KN64**	**Michele Pavone**	*Heterogeneous functional materials for post-Li energy storage devices, new insights and design principles from quantum chemistry*
11.45 - 12.00	**ELE_OR65**	**Ernestino Lufrano**	*Study of lithiated Nafion-based nanocomposites membranes as single lithium-ion conducting electrolytes for lithium batteries*
12.00 - 12.15	**ELE_OR66**	**Anna Mangini**	*Li-ion Batteries with Innovative Silicon Anodes: Study of Electrolytes Based on Carbonates*
12.15 - 12.30	**ELE_OR67**	**Alessandro Brilloni**	*Novel methods for increasing energy and reducing environmental impact of lithium batteries.*

ELE 10

09.30 - 10.00	**ELE_KN68**	**Tealdi Cristina**	*Fast but not so fast: can we improve intercalation in cathode materials for rechargeable batteries?*
10.00 - 10.15	**ELE_OR69**	**Toigo Christina**	*Rheological properties of aqueous sodium alginate slurries*
10.15 - 10.30	**ELE_OR70**	**Leonardo Sbrascini**	*Enhanced Performance of a Sustainable Si/C Anode for High Energy Density Lithium-ion Batteries*
10.30 - 10.45	**ELE_OR71**	**Daniele Versaci**	*Carbon nitride based double layer approach for enhancing Li-S battery performances*
10.45 - 11.00	**ELE_OR72**	**Hamideh Darjazi**	*Improvement of NMC layered cathode materials by combined doping/coating and evaluation of electronic-ionic transport properties by electrochemical impedance spectroscopy*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE_KN73**	**Teofilo Rojo**	*Recent progress in electrode materials for next generation sodium ion batteries*
11.45 - 12.00	**ELE_OR74**	**Giovanna Maresca**	*Sodium-conducting, ionic liquid electrolytes for Na battery systems*
12.00 - 12.15	**ELE_OR75**	**Shahid Khalid**	*Aqueous sodium battery enabled by super-concentrated binary electrolyte.*
12.15 - 12.30	**ELE_OR76**	**Michele Tribbia**	*Improved zinc electrodeposition in mild-acidic aqueous Zn-ion batteries*

Divisione TECNOLOGIA FARMACEUTICA (TFA)

TFA 03

09.30 - 10.00	**TFA IL005**	**Manuela Estima Gomes**	*Using magnetic stimulus to bioengineer tendon tissue and tissue models: new tools to understand and stimulate regenerative pathways*

21 settembre - mattina

10.00 - 10.30	**TFA IL006**	**Marco Romanelli**	*Inflammation in wound healing: the role of drug delivery*
10.30 - 10.45	**Discussion**		
10.45 - 11.00	**break**		
11.00 - 11.15	**TFA OR019**	**Giuseppina Sandri**	*Polysaccharides based scaffolds for skin tissue engineering*
11.15 - 11.30	**TFA OR020**	**Giulia Vanti**	*Development and Optimisation of a Locally- acting Microemulgel to Improve the Biopharmaceutical Properties of Cannabidiol for Dermatological Delivery*
11.30 - 11.45	**TFA OR021**	**Silvia Pisani**	*Engineered tubular scaffold for full-thickness esophageal replacement*
11.45 - 13.30	**Tavola Rotonda**	**Michele Schlich**	*Valorizzazione del dottorato in tecnologia farmaceutica al di fuori dell'accademia. Cosa si aspetta un’azienda da un dottore di ricerca rispetto ad un laureato?*

Programma dei LAVORI di DIVISIONE - 21 settembre pomeriggio

Divisione CHIMICA ANALITICA (ANA)

ANA10

15.00 - 15.20	**ANA PZ004**	**Martina Catani**	*Boosting the downstream processing of biopharmaceuticals by means of multicolumn continuous chromatography*
15.20 - 15.40	**ANA IL007**	**Maurizio Quinto**	*Rotating Magnetic Chromatography, a new technique for micro-particle and cell separation*
15.40 - 16.00	**ANA IL008**	**Roccaldo Sardella**	*Role of mobile phase composition in enantioselective liquid chromatography*
16.00 - 16.15	**ANA OR076**	**Federica Bianchi**	*Nanomaterials for improved sensitivity in sample treatment*
16.15 - 16.30	**ANA OR077**	**Irene Coralli**	*Secondary reactions in the analysis of microplastics by Py-GC-MS*
16.30 - 16.45	**ANA OR078**	**Simona Felletti**	*Investigation of the chemoselectivity of normal phase stationary phases towards the separation of cannabinoids*
16.45 - 17.00	**ANA OR079**	**Giuseppina Gullifa**	*Potential Health Impact Assessment of New Pocket Pen- Vaporizers: Vapor Characterization Using SPME-GC/MS*
17.00 - 17.15	**ANA OR080**	**Jacopo La Nasa**	*Analytical pyrolysis coupled with gas chromatography/mass spectrometry and solvent extraction for the characterization of microplastics and polymer additives*
17.15 - 17.30	**ANA OR081**	**Roberta La Tella**	*Evaluation of carbon - clad zirconia columns as stationary phases for superheated water liquid chromatography*
17.30 - 17.45	**ANA OR082**	**Marcello Locatelli**	*Fabric Phase Sorptive Extraction: an innovative tool for TDM and pharmacotoxicological studies using unconventional biological matrices*
17.45 - 18.00	**ANA OR083**	**Sara Palmieri**	*Molecular imprinted polymer coupled to LC-MS/MS for maleic hydrazide determination in food samples*
18.00 - 18.15	**ANA OR084**	**Marco Roverso**	*Determination of lactose in low-lactose milk by direct liquid injection and high-resolution mass spectrometry*

ANA11

15.20 - 15.40	**ANA KN010**	**Silvia Berto**	*Study and application of chemical models to measure the urine saturation with calcium salts*
15.40 - 16.00	**ANA OR085**	**Chiara Abate**	*Sequestering ability of carnosine towards some potentially toxic divalent metal cations in aqueous solution*

16.15 - 16.30	**ANA OR087**	**Denise Bellotti**	*Understanding the thermodynamics and coordination chemistry of metal-binding proteins: the common thread to elucidate metal acquisition processes at host/pathogen interface*
16.30 - 16.45	**ANA OR088**	**Rosita Cappai**	*Complex formation equilibria of a kojic acid derivative with different metal ions*
16.45 - 17.00	**ANA OR089**	**Salvatore Cataldo**	*CYCLODEXTRIN-BASED NANOSPONGES FOR LEAD(II) ION ADSORPTION FROM AQUEOUS SOLUTIONS*
17.00 - 17.15	**ANA OR090**	**Ottavia Giuffrè**	*O-phosphorylethanolamine and O-phosphorylcholine in aqueous solution: acid-base behavior and speciation with Mg2+*
17.15 - 17.30	**ANA OR091**	**Anna Irto**	*Thermodynamic parameters on the interaction of divalent and trivalent metal cations with 3-hydroxy-4-pyridinones*
17.30 - 17.45	**ANA OR092**	**Luana Malacaria**	*Studies on the complexation between quercetin and some first-row transition metal cations in aqueous solution*
17.45 - 18.00	**ANA OR093**	**Rossella Migliore**	*Recognition of antibiotics by calixarene-based micellar aggregates in aqueous solution: binding features and driving forces*
18.00 - 18.15	**ANA OR094**	**Davide Spanu**	*On-line ion trapping by frontal chromatography ICP-MS: a low-cost strategy for the fast speciation of inorganic pollutants*

ANA12

15.20 - 15.40	**ANA KN011**	**Flavio Della Pelle**	*2D Nanomaterials: among functional natural compounds and affordable sensor designs*
15.40 - 16.00	**ANA KN012**	**Barbara Roda**	*Celector(R): the cell chromatography for quality control of living cells*
16.00 - 16.15	**ANA OR095**	**Jessica Brandi**	*Identification of protein biomarkers responsible for meat tenderness in bovine Longissumus dorsi muscle by Kohonen self-organizing maps and multivariate analysis*
16.15 - 16.30	**ANA OR096**	**Simone Cavalera**	*Anti-Retroviral Drugs Monitoring in Urine and Saliva: A Rapid and Sensitive Lateral Flow Immunoassay for Tenofovir*
16.30 - 16.45	**ANA OR097**	**Andrea Cerrato**	*An innovative analytical platform for cannabis chemovar differentiation based on untargeted metabolomics and chemometrics*

16.45 - 17.00	**ANA OR098**	**Angela Di Capua**	*Use of online buffer exchange coupled to native-mass spectrometry to elucidate the stoichiometry of the Salmonella FraR (transcriptional repressor)-DNA complex*
17.00 - 17.15	**ANA OR099**	**Fabio Di Nardo**	*Exploiting silver nanoplates as colorimetric label in Lateral Flow Immunoassay*
17.15 - 17.30	**ANA OR100**	**Nicolò Interino**	*UPLC-Q-TOF-MS/MS analysis of bile acids and their main metabolite profile in farm animal faeces and species-specific correlation with gut microbiota*
17.30 - 17.45	**ANA OR101**	**Valentina Marassi**	*Nanosphere, polymer, self-assembled material? Clearing up the confusion on polydopamine through multidetection-FFF*
17.45 - 18.00	**ANA OR102**	**Monica Mattarozzi**	*Insights into aptamer-protein interactions for analytical applications: egg white lysozyme as case study*
18.00 - 18.15	**ANA OR103**	**Lapo Renai**	*Untargeted metabolomics reveals different postprandial serum metabolome profiles after single intake of Vaccinium myrtillus and Vaccinium corymbosum*

Divisione CHIMICA INDUSTRIALE (IND)
IND 04
Sessione congiunta con Gruppo Interdivisionale Green Chemistry - Chimica Sostenibile

15.00 - 15.20	**IND KN006**	**Rafael Luque**	*Benign by design strategies for a more sustainable future: the valorisation concept*
15.20 - 15.30	**IND OR049**	**Anna Gagliardi**	*Upgrading of Ethanol: Boosting the Guerbet Reaction with a Redox Co-Catalyst*
15.30 - 15.40	**IND OR050**	**Ilenia Rossetti**	*Sustainable process design for the valorization of bioethanol as platform chemical*
15.40 - 15.50	**IND OR051**	**Maela Manzoli**	*Enabling technologies to boost cellulose selective valorisation over bifunctional catalyst*
15.50 - 16.00	**IND OR052**	**Silvia Tabasso**	*Green deep eutectic solvents and microwave technology towards a closed loop biorefinery*
16.00 - 16.10	**IND OR053**	**Nicola Di Fidio**	*Microwave-assisted FeCl3-catalysed production of glucose from giant reed and cardoon cellulose fraction and its fermentation to new generation oil by oleaginous yeasts*
16.10 - 16.20	**IND OR054**	**Alessia Ventimiglia**	*Theoretical study of glucose oxidation to glucaric acid using gold based catalyst*
16.20 - 16.35	***Discussion***		
16.35 - 16.50	**break**		
16.50 - 17.10	**IND KN007**	**Volker Hessel**	*Sustainability as Process Design Guidance for Flow and Plasma Chemistry*
17.10 - 17.20	**IND OR055**	**Valeria Pappalardo**	*Heterogeneous catalysis in the esterification of natural antioxidants*

17.20 - 17.30	**IND OR056**	**Carmelina Rossano**	*Amberlite IR120 as catalyst for the levulinic acid esterification reaction in batch and continuous operation*
17.30 - 17.40	**IND OR057**	**Silvia Giorgi**	*Synthesis of new biopolymers by biomasses valorization*
17.40 - 17.50	**IND OR058**	**Riccardo Bacchiocchi**	*Innovative heterogeneous catalysts for the reduction of levulinic acid derivatives to γ-valerolactone and consecutive reduction products*
17.50 - 18.00	**IND OR059**	**Francesco Mauriello**	*Hydrogenolysis of aromatic ethers under lignin-first conditions*
18.00 - 18.30	**Discussion**		

Divisione CHIMICA ORGANICA (ORG)
ORG 15

15.00 - 15.30	**ORG PZ002**	**Paolo Tecilla**	***Medaglia Angelo Mangini*** *Self-organized Supramolecular Systems for Catalysis, Sensing and Transport*
15.30 - 16.00	**ORG PZ009**	**Elena Lenci**	***Premio alla ricerca Chimica Organica per le Scienze della Vita Junior*** *Combining Diversity-Oriented Synthesis and chemoinformatics to generate small molecules libraries*
15.50 - 16.00	**Break**		
16.00 - 16.15	**ORG OR092**	**Molly Pither**	*Elucidation of the Chemical Structure of Lipopolysaccharides Isolated from the Commensal Bacteria Veillonella parvula*
16.15 - 16.30	**ORG OR093**	**Debora Pratesi**	*The glycomimetic approach for selective inhibition of Carbonic Anhydrases*
16.30 - 16.45	**ORG OR094**	**Deborah Quaglio**	*Resorc[4]arene-based site directed immobilization of antibodies for immunosensors development*
16.45 - 17.00	**ORG OR095**	**Roberto Rossi**	*Problem solving in Pharmaceutical processes: isolation, characterization and synthetic preparation of unknown impurities in 4-piperidinepropanol manufacture*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR096**	**Laura Russo**	*Chemoselective synthesis of triple-functionalizes nanoparticles for multimodal in vivo imaging of pancreatic β-cells*
17.45 - 18.00	**ORG OR097**	**Giovanni Sacco**	*Affinity enhancement of peptide ligands for tumor overexpressed receptors*
18.00 - 18.15	**ORG OR098**	**Cristina Manuela Santi**	*Synthesis of an analogue of Neisseria meningitidis A capsular polysaccharide for the development of a glycoconjugate vaccine*
18.15 - 18.30	**ORG OR099**	**Federica Santino**	*Rational Design of Pseudoproline-Containing K-Opioid Receptor-Selective Peptidomimetics*

21 settembre - pomeriggio

ORG 16

15.30 - 16.00	**ORG PZ010**	**Manuel Orlandi**	***Premio alla ricerca Chimica Organica nei suoi Aspetti Metodologici Junior*** ***Catalyst Design via Computational Means:*** *Correlations Bridge Experiments and Calculations*
16.00 - 16.15	**ORG OR100**	**Valentina Pirota**	*Selective hydrolysis of water-soluble naphthalene diimides driven by core-substitution*
16.15 - 16.30	**ORG OR101**	**Simone Potenti**	*4-Fluorothreonine as a test case: the effects of fluorination on molecular properties*
16.30 - 16.45	**ORG OR102**	**Michele Ricci**	*Application of ASCA modelling tools on a PDO hard cheese: Analysis of the effects on physical parameters of Trentingrana*
16.45 - 17.00	**ORG OR103**	**Federica Sabuzi**	*Computational study of substituted phenols pKa*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR104**	**Carla Rizzo**	*New supramolecular fluorescent NDI-gels as bioimaging* *materials*
17.45 - 18.00	**ORG OR105**	**Maria Sologan**	*Functionalized gold nanoparticles for MRI applications*
18.00 - 18.15	**ORG OR106**	**Benedetta Maria Squeo**	*Thiophene substituted aza-BODIPY as promising metal-* *free, pure NIR emitter for OLEDs*
18.15 - 18.30	**ORG OR107**	**Kristian Vasa**	*Design and synthesis of macromolecular and nanostructured carbonic anhydrases-based materials*

ORG 17

15.30 - 16.00	**ORG PZ011**	**Sara Meninno**	***Premio alla ricerca Chimica Organica per l'Ambiente, l'Energia e le Nanoscienze Junior*** *Powerful Strategies to Functionalized Molecules in One- Pot, Mild Conditions and Benign Solvents*
16.00 - 16.15	**ORG OR108**	**Giulio Bertuzzi**	*Novel Visible-Light Mediated Protocols for the Synthesis* *of N Heterocycles and Site-Selective Functionalizations*
16.15 - 16.30	**ORG OR109**	**Tommaso Bortolato**	*Radical α-Trifluoromethoxylation of Ketones by Means of Organic Photoredox Catalysis*
16.30 - 16.45	**ORG OR110**	**Mattia Di Maro**	*A ball-milling green synthetic procedure for the preparation of novel macromolecular stabilizers for polyolefinic-based materials*
16.45 - 17.00	**ORG OR111**	**Salvatore Marullo**	*Cholinium-based ionic liquids as catalysts for the glycolysis of post-consumer PET waste*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR112**	**Angelica Mero**	*Treatment of biomass food waste by exploiting Natural Deep Eutectic Solvents and bio based-Ionic Liquids*

17.45 - 18.00	**ORG OR113**	**Elisabetta Monciatti**	*Hydroaminomethylation of terminal alkenes in water: microwave and micellar catalysis roles*
18.00 - 18.15	**ORG OR114**	**Matteo Tiecco**	*Organocatalytic activity of chiral L-Proline-based Deep Eutectic Solvents*
18.15 - 18.30	**ORG OR115**	**Federica Valentini**	*Catalytic biomass valorization towards hydrogen transfer reactions using formic acid and derivates as safe H-source*

ORG 18

15.30 - 16.00	**ORG PZ012**	**Nicolas D'Imperio**	***Premio alla ricerca Chimica Organica per lo Sviluppo di Processi e Prodotti nell' Industria Junior*** *Olefins from carbonyls. Development of new phosphorus-based cross-coupling reactions*
16.00 - 16.15	**ORG OR116**	**Valerio Fasano**	*How Big is the Pinacol Boronic Ester as a Substituent?*
16.15 - 16.30	**ORG OR117**	**Susanna Bertuletti**	*From carbonyls to chiral alcohols via asymmetric biocatalysis: exploiting the substrate promiscuity of hydroxysteroid dehydrogenases (HSDHs)*
16.30 - 16.45	**ORG OR118**	**Denisa Bisag**	*Catalyst- and substrate- dependent chemodivergent reactivity of stabilised sulfur ylides with salicylaldehydes*
16.45 - 17.00	**ORG OR119**	**Giulia Brufani**	*Imidazolium based heterogenous catalyst for the synthesis of cyanohydrintrimethylsylil ether and β-azido ketones*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR120**	**Emanuela Calcio Gaudino**	*Highly Efficient Microwave-assisted synthetic protocols under Pd based β-cyclodextrin heterogeneous catalyst*
17.45 - 18.00	**ORG OR121**	**Francesco Calogero**	*Photoredox allylation and propargylation of aldehydes catalytic in titanium*
18.00 - 18.15	**ORG OR122**	**Vincenzo Campisciano**	*Al(III) Porphyrin–Imidazolium Salt Copolymer onto Carbon Nanotubes as Catalyst for the Synthesis of Cyclic Carbonates*
18.15 - 18.30	**ORG OR123**	**Francesca Foschi**	*Copper-Catalyzed/Hypervalent Iodine(III)-Mediated Dimerization/Cyclization of 2-Benzylamino-phenols: Synthesis of Fluorescent Oxazolo-phenoxazines*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 04

15.00 - 15.30	**CSB KN005**	**Angela Casini**	*Gold-templated reactions in biological systems: from medicine to catalysis*

15.30 - 15.45	**CSB OR022**	**Francesco Bellia**	*Hyaluronate–Carnosine conjugates: copper(II) complexes and antioxidant properties*
15.45 - 16.00	**CSB OR023**	**Daniele Vitone**	*The speciation of zinc complexes with chloroquine ligand*
16.00 - 16.15	**CSB OR024**	**Valentina Oliveri**	*8-Hydroxyquinoline Hybrids Differentially Interact with α-Synuclein*
16.15 - 16.30	**CSB OR025**	**Giancarlo Terraneo**	*Halogenation Dictates Architectures and Properties of Amyloid Peptides*
16.30 - 17.00	**Break**		
17.00 - 17.30	**CSB KN006**	**Amedeo Caflisch**	*Fragment-based drug design*
17.30 - 17.45	**FIS OR066**	**Federica Rizzi**	*Role of the FZD10 delivering exosomes in cellular proliferation of gastrointestinal cancer*
17.45 - 18.00	**FIS OR062**	**Ivana Miletto**	*Functionalized Upconversion Nanoparticles for Theranostic*
18.00 - 18.15	**CSB OR028**	**Gabriele Travagliante**	*Spectroscopic study on interactions of porphyrins and micro-RNA*
18.15 - 18.50	**Discussione**		

Divisione DIDATTICA CHIMICA (DID)
DID 03

15:00-15:30	**DID IL003**	**Eleonora Aquilini**	*Caring for yourself, the environment and others in primary school*
15:30-15:45	**DID OR014**	**Sergio Palazzi**	*Towards a material archive of dyestuffs from the XX century*
15:45-16:00	**DID OR015**	**Ugo Cosentino**	*The School-University joint interventions provided in the National Recovery and Resilience Plan*
16:00-18:00	**Panel Discussion**	**Riccardo Iacona (Coordinator)** **Vincenzo Balzani** **Andrea Segrè** **Vittorio Maglia** **Giovanni De Feo**	*360-degree sustainability*

Divisione SPETTROMETRIA DI MASSA (MAS)
MAS 03

15.00 - 15.40	**MAS PL004**	**Encarnación Moyano**	*Mass spectrometry for the environmental analysis of halogenated organic pollutants*
15.40 - 16.10	**MAS KN003**	**Sara Bogialli**	*Mass spectrometry for the monitoring and protection of the environment*
16.10 - 16.25	**MAS OR011**	**Carolina Barola**	*Temporal trend of per- and polyfluoroalkyl substances in air samples collected at the rural site of Monte Martano (Central Italy)*
16.25 - 16.35	**Break**		

21 settembre - pomeriggio

16.35 - 17.15	**MAS PL005**	**Antony Memboeuf**	*How can energetics in CID MS/MS help the analytical chemists?*
17.15 - 17.30	**MAS OR012**	**Angela Tartaglia**	*Fabric Phase Sorptive Membrane Array: A Novel Approach for Non-Invasive In Vivo Sampling*
17.30 - 17.45	**MAS OR013**	**Raffaella Pascale**	*An interplay between FT-ICR MS and LC-LTQ MS/MS for Metabolic Profiling of Peperoni di Senise PGI Bell Peppers*
17.45 - 18.00	**MAS OR014**	**Eugenio Aprea**	*Volatile organic compounds in Gorgonzola cheese and their relationship with sensory descriptors and consumers' liking*
18.00 - 18.15	**MAS OR015**	**Flaminia Vincenti**	*New Synthetic Opioids: Development of Analytical Methods for Their Characterization and Determination by Means of HPLC-HRMS/MS*

Divisione TEORICA E COMPUTAZIONALE (TEO)

TEO 04

15:00 -15:20	**TEO KN004**	**Mauro Stener**	*Predictive optical photoabsorption of metal clusters via efficient TDDFT simulations*
15:20 - 15:40	**TEO PZ005**	**Lorenzo Cupellini**	*Multiscale investigation of chlorophyll fluorescence quenching in plant light-harvesting complexes*
15:40 - 15:50	**TEO OR024**	**Chiara Aieta**	*Quantum nuclear densities from semiclassical on-the-fly molecular dynamics*
15:50 - 16:00	**TEO OR025**	**Filippo Lipparini**	*An easy and efficient strategy to compute an accurate SCF guess for ab-initio molecular dynamics simulations*
16:00 - 16:10	**TEO OR026**	**Marco Mendolicchio**	*Accuracy and Reliability in the Simulation of Vibrational Spectra: A Comprehensive Benchmark of Generalized Vibrational Perturbation Theory to the Second Order (GVPT2)*
16:10 - 16:20	**TEO OR027**	**Fulvio Perrella**	*Improving accuracy and efficiency of ADMP Extended Lagrangian Molecular Dynamics*
16:20 - 16:30	**TEO OR028**	**Diego Sorbelli**	*Probing the electronic structure of gold dihydride with state-of-the-art relativistic approaches*
16:30 - 17:00	**break**		
17:00 - 17:20	**TEO PZ006**	**Nicola Tasinato**	*Computational Strategies for Environmental Chemistry*
17:20 - 17:30	**TEO OR029**	**Francesco Di Maiolo**	*Theoretical Approaches to Quantum Molecular Dynamics in Out of Equilibrium Environments*
17:30 - 17:40	**TEO OR030**	**Lorenzo Donà**	*Extending and assessing composite electronic structure methods to the solid state*
17:40 - 17:50	**TEO OR031**	**Federica Lodesani**	*An in-depth look into the mechanism of crystallization of lithium disilicate: a metadynamics study*

21 settembre - pomeriggio

17:50 - 18:00	**TEO OR032**	**D. K. Andrea Phan Huu**	*Molecular spectroscopy in condensed phases: an antiadiabatic approach to the medium polarizability*
18:00 - 18:10	**TEO OR033**	**Pierpaolo Pravatto**	*Tunneling splitting and the stochastic description of activated processes*
18:10 - 18:30	**discussione finale**		

Programma dei LAVORI di DIVISIONE - 23 settembre mattina

Divisione CHIMICA ANALITICA (ANA)

ANA13

09.30 - 09.50	**ANA IL009**	**Anna Laura Capriotti**	*The progress in peptidomics: new strategies for purification and untargeted identification of short peptides*
09.50 - 10.00	**break**		
10.00 - 10.15	**ANA OR104**	**Adriana Arigò**	*Analytical methods in clinical lipidomics: HPLC and SFC comparison for the analysis of lipid mediators in clinical samples*
10.15 - 10.30	**ANA OR105**	**Alfonsina D'Amato**	*nLC-MS/MS data integration of quantitative proteomics and lipidomics to study the effects of bioactive compounds*
10.30 - 10.45	**ANA OR106**	**Chiara De Luca**	*Multicolumn Countercurrent Solvent Gradient Purification (MCSGP) process for the intensification of the polishing step of a bioactive peptide mixture*
10.45 - 11.00	**ANA OR107**	**Dounia El Fadil**	*Enzyme inhibition coupled to Molecular Imprinted Polymers for acetazolamide determination in biological samples*
11.00 - 11.15	**ANA OR108**	**Alessio Lenzi**	*Determination of salivary short chain fatty acids and hydroxy acids in heart failure patients by in-situ derivatization and Hisorb-probe sorptive extraction coupled to thermal desorption and gas chromatography- tandem mass spectrometry*
11.15 - 11.30	**ANA OR109**	**Marcello Manfredi**	*Metaproteomics and metabolomics investigation of microbiome alterations in pediatric obese subjects*
11.30 - 11.45	**ANA OR110**	**Francesca Merlo**	*A simple and Fast Multiresidue Method for determination of hormones in vegetables and fruits*
11.45 - 12.00	**ANA OR111**	**Giuseppe Micalizzi**	*Microwave distillation technique for the isolation of Cannabis Sativa L. essential oils and GC-MS/FID analysis for terpenes and terpenoids characterization.*
12.00 - 12.15	**ANA OR112**	**Daniele Naviglio**	*“Cholesterol is not considered a nutrient of concern for overconsumption” (Dietary Guidelines for Americans 2015)*

ANA14

09.30 - 09.50	**ANA IL010**	**Nicola Cioffi**	*Analytical Challenges in the Fight Against Biological Threats. The case of Nanoantimicrobials Inhibiting the Persistency of SARS-CoV-2*
09.50 - 10.00	**break**	**break**	
10.00 - 10.15	**ANA OR113**	**Maria Luisa Astolfi**	*A rapid analytical method for the determination of 45 elements in extra-virgin olive oils*

10.15 - 10.30	**ANA OR114**	**Laura Barone**	*Innovative spectroscopic approach for bloodstains identification*
10.30 - 10.45	**ANA OR115**	**Deborah Biggio**	*Surface characterization of CuZn37 alloys in contact with artificial saliva: the role of organic compounds*
10.45 - 11.00	**ANA OR116**	**Beatrice Campanella**	*A multi-analytical approach for the study of immortalized hippocampal neurons after mild heat shock*
11.00 - 11.15	**ANA OR117**	**Roberta D'Agata**	*Ultrasensitive plasmonic assay and specifically-designed PNA probes for circulating microRNAs detection: towards a liquid biopsy*
11.15 - 11.30	**ANA OR118**	**Danilo Donnarumma**	*Identification and quantification of toxic compounds and essential molecules in the context of tuna fishery industry waste valorization*
11.30 - 11.45	**ANA OR119**	**Walter Giurlani**	*Film thickness determination of metal multilayers by XRF multivariate analysis using Monte Carlo simulated standards*
11.45 - 12.00	**ANA OR120**	**Giulia Gorla**	*Low-cost miniaturized NIR spectrometer as an analytical tool for monitoring kefir fermentation process*
12.00 - 12.15	**ANA OR121**	**Min Li**	*XAS study of Manganese Hexacyanoferrate cathode material in aqueous Zn-ion batteries at three K-metal edges*
12.15 - 12.30	**ANA OR122**	**Maria Chiara Sportelli**	*Analytical characterization of laser-ablated silver nanoparticles for safe and biodegradable food packaging applications*

ANA15

09.30 - 09.50	**ANA OR123**	**Raffaela Biesuz**	*SAFER Smart Labels at work on fish*
09.50 - 10.00	**break**		
10.00 - 10.15	**ANA OR124**	**Sara Gaggiotti**	*Liquid phase exfoliated Transition Metal Dichalcogenides for gas sensing*
10.15 - 10.30	**ANA OR125**	**Laura Montali**	*A clover-like paper biosensor for mercury (II) on-site monitoring with a combined bioluminescent-colorimetric detection*
10.30 - 10.45	**ANA OR126**	**Andrea Pastore**	*pH Colorimetric sensor Arrays based on acid-base indicators enhanced by surfactants*
10.45 - 11.00	**ANA OR127**	**Angela Punzo**	*Application of whole-cell analytical bioassay based on turn-on chemiluminescence dioxetane probe sensing to quantify intracellular H2O2 in nutraceutical and biomedical fields*
11.00 - 11.15	**ANA OR128**	**Simona Ranallo**	*Non-natural antibody-protein communication mediated by a synthetic DNA responsive device*

23 settembre - mattina

11.15 - 11.30	**ANA OR129**	**Annalisa Scroccarello**	*Colorimetric paper-based analytical device for direct evaluation of olive oil phenols*
11.30 - 11.45	**ANA OR130**	**Francesca Torrini**	*A competitive microplate bioassay to detect gonadorelin in urine samples via a polynorepinephrine-based molecular imprinted polymer*
11.45 - 12.00	**ANA OR131**	**Mohamad Ahmad**	*A spatial perspective to retrieve spatial-spectral signatures from overlapped components in spectroscopic imaging data*
12.00 - 12.15	**ANA OR132**	**Rosalba Calvini**	*Quantification of rind percentage in grated Parmigiano Reggiano cheese by NIR-hyperspectral imaging and evaluation of the effect of factors related to sample preparation and composition*
12.15 - 12.30	**ANA OR133**	**Eleonora Mustorgi**	*Multivariate online monitoring of a powder blending process using a miniaturized near infrared sensor*

Divisione CHIMICA FISICA (FIS)

FIS 10

Physical Chemistry of Biomaterials

09:30-10:00	**FIS KN012**	**Roberto De Santis**	*Design for biointerface engineering*
10:00-10:30	**FIS KN013**	**Julietta Rau**	*New trends in the development of biomedical implants with multifunctional surfaces*
10:30-10.45	**FIS OR096**	**Monica Dettin**	*Chitosan covalently functionalized with peptides mapped on Vitronectin and BMP-2 for bone tissue engineering*
10:45-11:00	**FIS OR097**	**Angela De Bonis**	*Study of the bioactivity of thin glass-ceramic films deposited on electrospun polymeric scaffolds by nanosecond PLD*
11:00-11.15	**FIS OR021**	**Lorenzo Degli Esposti**	*Crystallization of amorphous calcium phosphate to hydroxyapatite nanoparticles: new insights in the field of biomaterials and biomineralization*
11:15-11.30	**FIS OR099**	**Alessio Carmignani**	*Study of the impact of size on the properties of polydopamine nanoparticles and their interaction with glioblastoma multiforme cells*

Computational and Applied Chemistry

11.45-12.00	**FIS OR100**	**Laura Orian**	*Methylmercury toxicity: insight from a theoretical physical-chemical description*
12:00_12:15	**FIS OR101**	**Marta Corno**	*Ab-initio modelling of Fe2NiP-H2O interaction: a phosphate factory for Early Earth*
12:15-12.30	**FIS OR102**	**Mirko Leccese**	*First-principles study of the C/Si interface: the influence of graphene corrugation on the H adsorption and abstraction reactions*

12:30-12:45	**FIS OR103**	**Brunella Bardi**	*Excited-state symmetry breaking in an aza-nanographene dye*
12:45-13:00	**FIS OR104**	**Rosangela Santalucia**	*HCN adsorption and reactivity at the Mg_2SiO_4 surface:a laboratory model of the chemistry on interstellar dust grains*

FIS 11

Physical Chemistry for Environment and Materials I

09:30-10:00	**FIS KN014**	**Cataldo Simari**	*Reversible and low-cost CO_2 capture by quaternary-ammonium-functionalized aromatic polymers*
10:00-10:15	**FIS OR105**	**Claudio Cara**	*High value-added mesostructured silica from hexafluorosilicic acid (FSA): from a hazardous waste to precious silicon source.*
10:15-10.30	**FIS OR106**	**Rodolfo Esposito**	*A sustainable approach to formulation chemistry:structure and dynamics of bio-based complex mixtures*
10:30-10.45	**FIS OR107**	**Mariafrancesca Baratta**	*Photocatalytic degradation of organic pollutants in water using an innovative TiO_2/SWNT membrane*
10:45-11:00	**FIS OR108**	**Chiara Lo Porto**	*Plasma deposition of TiO_2-based nanocomposite coating for photocatalytic degradation of organic pollutants in water*
11:00-11.15	**FIS OR110**	**Stefano Marchesi**	*The NMR relaxometry as a powerful tool to study the uptake of paramagnetic ions from water by synthetic saponite clays*
11:15-11.30	**FIS OR109**	**Giulia Siciliano**	*Synthesis and characterization of polydopamine coated SPIONs for Cu^{2+} ions removal of from water*
11.30-11.45	**break**		

Physical Chemistry for Environment and Materials II

11:45-12:00	**FIS OR111**	**Nicola Blangetti**	*Template assisted sol-gel synthesis of Fe-doped TiO_2 with photocatalytic activity under visible light*
12:00_12:15	**FIS OR112**	**Chiara Nannuzzi**	*Physico-chemical characterization of high surface area TiO_2*
12:15-12.30	**FIS OR113**	**Massimo Dell'Edera**	*Nano-TiO_2 based material for environmental and antibacterial application*
12:30-12:45	**FIS OR114**	**Marco Montalbano**	*Combining Morphology, Surface Fluorination and Au Nanoparticles Deposition on TiO_2: Effects on Rhodamine B Photodegradation*
12:45-13:00	**FIS OR115**	**Maria Francesca Colella**	*Chemical-physical methods to investigate properties of vegetable oils and fats*
13:00-13:30	***Conclusioni***		

FIS 12

Thermodynamics and Kinetics I

09:30-10:00	**FIS KN015**	**Andrea Scorciapino**	*Development of a thermodynamic and kinetic model for passivemigration of ion carriers across lipid bilayers*
10:00-10:15	**FIS OR116**	**Marco Paolantoni**	*When the Solute is Completely Slaved to the Solvent:Jump Reorientation of Formamide in Water*
10:15-10.30	**FIS OR117**	**Federico Rossi**	*Shape Transformation of Artificial Vesicles Induced by an Interplay between Osmosis and pH Change*
10:30-10.45	**FIS OR118**	**Martina Maria Calvino**	*Shelf-life prediction of paracetamol formulations by non-isothermal thermogravimetry*
10:45-11:00	**FIS OR119**	**Chiara Pelosi**	*Stability of protein-polymer conjugates in solution*
11:00-11.15	**FIS OR120**	**Stefano Salvestrini**	*Kinetics and mechanism of 4-hydroxybenzoic acid degradation by persulfate/MnO2 oxidation*
11:15-11.30	**FIS OR121**	**Valentina Migliorati**	*Unraveling the solvation properties of Lanthanide (3+) ions: from molecular solvents to Ionic Liquid based systems*

Thermodynamics and Kinetics II

11:45-12:00	**FIS OR122**	**Marcello Budroni**	*Between dissipative structure and applications: chemical oscillations*
12:00_12:15	**FIS OR123**	**Olga Russina**	*NATURE OF SOLVATION OF CYCLODEXTRINS IN (PROTIC) IONIC LIQUIDS AND DEEP EUTECTIC SOLVENTS*
12:15-12.30	**FIS OR124**	**Duccio Tatini**	*Specific ions effects in green oleate-based formulations: how salts can influence the structure and rheology of viscoelastic systems*
12:30-12:45	**FIS OR125**	**Marianne Moedlinger**	*Structures and phase equilibria in the ternary Cu-As-Sb system (a preliminary investigation)*
12:45-13:00	**FIS OR126**	**Alessandro Damin**	*Cu+ bi-pyridine based homoleptic complexes as catalysts for partial oxidation reactions: a Raman study*

Divisione CHIMICA INDUSTRIALE (IND)
IND 06

09.30 - 10.00	**IND KN008 Medaglia Mario Giacomo Levi**	**Siglinda Perathoner Gaetano Iaquaniello**	*Waste-to-chemicals: a low-carbon innovative solution for circularity*
10.00 - 10.10	**IND OR060**	**Stefania Lucantonio**	*Experimental study of interactions between biomass pellets and oxygen carriers for chemical looping gasification in fluidized beds*

10.10 - 10.20	**IND OR061**	**Lucia Fagiolari**	*Electrodes and electrolytes for aqueous dye-sensitized solar cell*
10.20 - 10.30	**IND OR062**	**Francesca Rosso**	*Carbon Dioxide Absorption Mechanism in Biocompatible Ionic Liquids Solutions*
10.30 - 10.40	**IND OR063**	**Giuliano Giambastiani**	*“To Dissipate or not to Dissipate extra-Heat? This Is the Question!” How to Reduce Energy Wastes in a Challenging Process at the Heart of P2G Chain*
10.40 - 10.50	**IND OR064**	**Matteo Borella**	*A study of Kraft lignin conversion and possible upgrading to valuable compounds*
10.50 - 11.05	***Discussion***		
11.05 - 11.20	**break**		
11.20 - 11.40	**IND KN009**	**Paolo Vacca**	*New generation of specialty zeolites for sustainable chemistry*
11.40 - 11.50	**IND OR065**	**Giorgio Ferrari**	*Multifunctional Hardening Accelerator for Low-Clinker Binders*
11.50 - 12.00	**IND OR066**	**Rosa Vitiello**	*Optimization of HASE polymers effect in formulation of cement using Design of Experiment*
12.00 - 12.10	**IND OR067**	**Matteo Guidotti**	*Are Aqueous Hydrogen Peroxide and Sodium Percarbonate Efficient in the Inactivation of SARS-CoV 2?*
12.10 - 12.20	**IND OR068**	**Carlo Pirola**	*Chemical Plants Active Learning by Virtual Immersive Laboratory: the Eye4edu Project*
12.20 - 12.30	**IND OR069** **Premio Tesi di Dottorato**	**Veronica Papa**	*Manganese- and Cobalt Based Catalysts for Homogeneous Hydrogenation*
12.30 - 12.40	**IND OR070**	**Elena Ghedini**	*Biomasses, Drug Delivery and Hi-Tech formulative protocols*
12.40 - 12.50	**IND OR071**	**Maryam Hmoudah**	*Assessment of the robustness of iron-based metal organic framework (MIL-88A) in aqueous environment*
12.50 - 13.00	***Discussion***		

Divisione CHIMICA INORGANICA (INO)

INO 10

9.30 - 10.00	**INO PZ009** **(Premio Malatesta)**	**Roberta Sessoli**	*The contribution of coordination chemistry to the second quantum revolution*
10.00 - 10.30	**INO PZ010** **(Premio Nasini 2021)**	**Edoardo Mosconi**	*Computational Modeling of Perovskite for Photovoltaic Applications*
10.30 - 10.45	**INO OR064-ad hoc**	**Iole Venditti**	*Functionalized silver nanoparticles for water pollution monitoring: sensitivity, selectivity and the challenge of eco-safe behavior*

23 settembre - mattina

10.45 - 11.00	**INO OR065**	**Diego Tesauro**	*New aromatic NHC-gold complexes as anticancer agents: protein target evaluation and cytotoxic activity*
11.00 - 11.15	**INO OR066**	**Farid Hajareh Haghighi**	*Silane-functionalized TiO2 nanoparticles decorated with Ag nanoparticles for dual antimicrobial effects*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR067**	**Francesca Tessore**	*Porphyrins for second order nonlinear optics*
11.45 - 12.00	**INO OR068**	**Annaluisa Mariconda**	*Sulfonated N-heterocyclic carbene silver(I) and gold(I) water soluble complexes: catalytic and cytotoxic activity*
12.00 - 12.15	**INO OR069**	**Riccardo Freccero**	*Widening the tin solid-state chemistry: unusual bonding scenario in the LaMgSn2 rare-earth stannide*
12.15 - 12.30	**INO OR070**	**Veronica Ghini**	*NMR reveals the metabolic changes induced by Auranofin in ovarian cancer cells*
12.30 - 13.00	**INO IL003**	**David P. Giedroc**	*Metals, molecules and metabolism: Molecular mechanisms of bacterial metallostasis*

INO 11

10.30 - 10.45	**INO OR071**	**Antonio Zucca**	*Advances in Pt(II) rollover chemistry*
10.45 - 11.00	**INO OR072**	**Marco Lunardon**	*Hybrid transition metal dichalcogenide/graphene microspheres for hydrogen evolution reaction*
11.00 - 11.15	**INO OR073**	**Silvia Mostoni**	*Porphyrin functionalized ZnO/SiO2 hybrid nanoparticles as scintillator agent*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR074**	**Alfonso Annunziata**	*Square-planar vs. trigonal bipyramidal molecular geometry in glucoconjugate triazole Pt(II) complexes: synthesis, in-solution behaviour and anticancer properties*
11.45 - 12.00	**INO OR075**	**Giada Mannias**	*Iron(III) trimesate xerogel by ultrasonic irradiation*
12.00 - 12.15	**INO OR076**	**Christian Rossi**	*Exploiting the transformative features of metal halides for the synthesis of CsPbBr3@SiO2 core-shell nanocrystals*
12.15 - 12.30	**INO OR077**	**Luciano Marchiò**	*Supramolecular assemblies in silver bispyrazolylmethane complexes: phase transitions and the role of the halogen bond*

INO 12

10.30 - 10.45	**INO OR078**	**Adolfo Speghini**	*Fine-tuning of the size of luminescent CaF2 nanoparticles*
10.45 - 11.00	**INO OR079**	**Antonio Santoro**	*Responsive Self-Assembled Dynamic Helicates*
11.00 - 11.15	**INO OR080**	**Chiara Mazzariol**	*Synthesis in confined space of luminescent nanostructures of undoped and Eu(III)-doped calcium molybdate*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR081**	**Marta Stucchi**	*The synergistic and photochromic effect of Au nanoparticles on a Silver-waste derived TiO2 photocatalyst*

11.45 - 12.00	**INO OR082**	**Diego Olivieri**	*Efficient palladium catalyzed bis-alkoxycarbonylation of olefins for the synthesis of useful succinic acid derivatives*
12.00 - 12.15	**INO OR083**	**Luca Rigamonti**	*Multivariate approach to the analysis of structural data of iron(II) spin crossover complexes and cobalt(II) single molecule magnets*
12.15 - 12.30	**INO OR084**	**Simonetta Geninatti**	*Histidine containing PLGA nanoparticles as novel theranostic agents for Boron Neutron Capture Therapy*

Divisione CHIMICA ORGANICA (ORG)

ORG 19

9.30 - 10.00	**ORG PZ003**	**Pierangelo Metrangolo**	***Medaglia Giorgio Modena*** *A Journey through the Word of Halogen Bonding*
10.00 - 10.30	**ORG PZ008**	**Jacopo Roletto**	***Premio alla ricerca Chimica Organica per lo Sviluppo di Processi e Prodotti nell'Industria*** *The art of Process Development in API manufacturing*
10.30 - 10.45	**ORG OR124**	**Andrea Sartori**	*Dual Conjugates Targeting αVβ3/αVβ6 Integrins and Tyrosine Kinase Receptors as antifibrotic agents*
10.45 - 11.00	**ORG OR125**	**Angela Scala**	*Synthesis and biological profile of novel three-arms star-shaped PLA-PEG amphiphilic copolymers*
11.00 - 11.15	**ORG OR126**	**Monica Scognamiglio**	*Isolation and structural elucidation of oleanane saponins from Bellis sylvestris Cyr. involved in plant-plant chemical interactions*
11.15 - 11.30	**ORG OR127**	**Alba Silipo**	*Herbaspirillum Root189 LPS glycan chain decorations affect LPS bioactivity, membrane properties and prevent plant immune recognition*
11.30 - 12.00	**Break**		
12.00 - 12.15	**ORG OR128**	**Laura Siracusa**	*Secondary metabolic profiles and anticancer actions from fruit extracts of immature pomegranates*
12.15 - 12.30	**ORG OR129**	**Rachele Stefania**	*Enhanced relaxivity by hydrophobic interactions of macrocyclic Gd-HPDO3A complexes linked to pyranine*
12.30 - 12.45	**ORG OR130**	**Luca Valgimigli**	*Oxygen Uptake Kinetics as a Powerful Tool to Investigate Tyrosinase Enzyme Inhibition*
12.45 - 13.00	**ORG OR131**	**Danilo Vona**	*Enzyme immobilization on polydopamine-coated living microalgae cells for bioremediation*

ORG 20

10.30 - 10.45	**ORG OR132**	**Matteo Corrieri**	*Metal-Free Synthesis of Azacarbolines Enabled by Hypervalent Iodine-Promoted Intramolecular Oxidative Cyclization*

23 settembre - mattina

10.45 - 11.00	**ORG OR133**	**Federico Frateloreto**	*Functionalization of C-H bond using self-assembling supramolecular iron(II) complexes*
11.00 - 11.15	**ORG OR134**	**Andrea Gualandi**	*Photoredox allylation of aldehydes mediated by bismuth and cobalt*
11.15 - 11.30	**ORG OR135**	**Marco Lombardo**	*Visible Light Photocatalytic Synthesis of Oxygenated Heterocyclic Compounds*
11.30 - 12.00	**Break**		
12.00 - 12.15	**ORG OR136**	**Michela Lupi**	*A Hydrogen Bond Donor / Lewis Base (HBD/LB) catalytic route to enantioenriched hetero[4]helicenes*
12.15 - 12.30	**ORG OR137**	**Giulia Martelli**	*Fast Heck-Cassar-Sonogashira Cross-Coupling Reactions with Palladium Catalyst Recycling and Green Solvent/Base recovery*
12.30 - 12.45	**ORG OR138**	**Silvia Gazzola**	*2- and 6-Purinylmagnesium Halides in Dichloromethane: Scope and Insights Into the Solvent Influence on the C- Mg Bond*
12.45 - 13.00	**ORG OR139**	**Angelo Nacci**	*Nanostructured catalysts for a circular economy*

ORG 21

10.30 - 10.45	**ORG PZ015**	**Gabriele Laudadio**	***Premio Tesi di Dottorato Chimica Organica nei suoi Aspetti Metodologici*** *New synthetic methods enabled by photochemistry and electrochemistry in flow*
10.45 - 11.00	**ORG OR140**	**Andrea Francesca Quivelli**	*Mild Approaches for Copper-Catalysed Coupling Reactions: Ligand-Free Ullmann-type C–N and C–O Bond Formation in Deep Eutectic Solvents*
11.00 - 11.15	**ORG OR141**	**Marco Rabuffetti**	*Stereoselective monoreduction of bulky 1,2-dicarbonyls catalyzed by a benzyl reductase from Pichia glucozyma (KRED1-Pglu)*
11.15 - 11.30	**ORG OR142**	**Daniele Ragno**	*Regiodivergent Isosorbide Acylation by Oxidative NHC-Catalysis in Batch and Continuous-Flow*
11.30 - 12.00	**Break**		
12.00 - 12.15	**ORG OR143**	**Giorgio Rizzo**	*Palladium anchored on Silk Fibroin as suitable catalyst for Suzuki-Miyaura Cross-Coupling Reactions*
12.15 - 12.30	**ORG OR144**	**Patrizio Russo**	*Novel Synthesis of Thienofuranone Derivates by Pd-Catalyzed Carbonylation Reaction*
12.30 - 12.45	**ORG OR145**	**Gabriele Lupidi**	*Vitamin B2 Promoted Tandem Nef-Henry Reactions for the synthesis of Symmetrical β-Nitro Alcohols from Nitroalkanes*

12.45 - 13.00	**ORG OR146**	**Ida Ziccarelli**	*Synthesis of Isobenzofuranones, Isochromenones and Thienopyranones by a Pd-Catalyzed Oxidative Carbonylation Approach*

PLENARY

The Lithium Battery, from a Dream to Readiness to take on Climate Change – Opportunities and Challenges for Chemists

M. Stanley Whittingham FRS

Chemistry Department, Binghamton University (SUNY), Binghamton, NY 13902-6000, USA

Lithium batteries have come from an idea in 1972 to dominate electrochemical energy storage today. They are now in a position to enable the large-scale introduction of renewable energy, as well as electrifying transportation, which will leave a cleaner and more sustainable environment for the next generation. There are ample scientific opportunities for chemists to further improve their performance, cost and safety. Today's cells attain only 25% of their theoretical energy densities, consume more than 50 kWh of power to make a 1 kWh battery, and use unsustainable and high cost components. As the energy density increases, safety tends to be compromised. Examples will include: the soft TiS_2 lattice, the layered oxides, $LiMO_2$, and Li_2VOPO_4; the last, a proof of concept for a two-electron transfer cathode. The opportunities and the technical challenges that need to be overcome will be described in order to open up a discussion.

Diffusion and Reaction in Small and Heterogeneous Systems

Ralf Metzler

Institute for Physics & Astronomy, University of Potsdam-Golm, Germany

Brownian motion is a ubiquitous phenomenon at the heart of non-equilibrium statistical mechanics and physical chemistry. Based on its theoretical description in terms of the diffusion equation, Smoluchowski calculated the diffusion limitation of molecular reactions in 1916. Today, by means of super resolution microscopy scientists can resolve the production and distribution of individual proteins and visualise how microbeads or fluorescently labelled molecules diffuse in a living biological cell. These experimental observations show that new theoretical models are needed to understand how transport and regulation wonks io systems such as live cells or their organisations in biofilms.

In my talk I will address two main lines of investigation. One is based on the fact that many molecular signalling reactions running off in cells are involving minute chemical concentrations. The resulting reaction dynamics then spans several decades of reactions times, and the meaning of chemical rates needs to be re-assessed. In particular I will introduce the concepts of geometry- and reaction-control of molecular reactions.

The second topic is the diffusive spreading itself, of tracer particles in complex, heterogeneous environments such as biological cells. A growing body o* experiments demonstrate that heterogeneity effects cause pronounced deviations from the Gaussian displacement distribution, the central law in statistical mechanics. I will highlight several experimental examples for non-Gaussian processes and present simple theoretical concepts for their description.

Discovery and Development of Non-hormonal Male Contraceptive Agents

Gunda I. Georg

Department of Medicinal Chemistry, College of Pharmacy, University of Minnesota, U.S.A.

There is a global need for novel contraceptive methods because worldwide about 40% of pregnancies are still unintended, about 42 million pregnancies are terminated by abortion, and 658 women per day die of pregnancy-related problems in the US (CDC 2020). While many contraceptive options exist for women, fewer are available for men. Testosterone-based contraceptives for men have been investigated for 60 years but challenges remain for commercialization. For these reasons and to provide couples with additional safe and reversible options for contraception, the development of non-hormonal contraceptives for both men and women is highly desirable to assist with family planning and reduce unintended pregnancies. Advances in the understanding of reproductive biology have provided many testis-specific targets that are under investigation for the discovery and development of a male contraceptive agent. However, developing agents that are highly effective, safe and completely reversible is a very significant challenge. Recent progress on the discovery of selective inhibitors of Na,K-ATPase-α4 based on the natural product ouabain [1, 2] and the antihistamine cetirizine will be presented. This enzyme is critical for sperm motility and hypermotility. In addition, recent progress on the development of a selective retinoic acid receptor-α antagonist for male contraception that reduce sperm counts will be discussed [3].

[1] Syeda, S. S.; Sánchez, G.; Hong, K. H.; Hawkinson, J.; Georg, G. I.; Blanco, G. Design, Synthesis, In Vitro and In Vivo Evaluation of Ouabain Analogs as Potent and Selective Na,K-ATPase α4 Isoform Inhibitors for Male Contraception. *J. Med. Chem.* **2018**, *61*, 1800-1820.
[2] Syeda, S, S.; Sánchez, G.; McDermott, J.; Hong, K. H.; Blanco, G.; Georg, G. I**.** The Na^+ and K^+ Transport System of Sperm (ATP1A4) is Essential for Male Fertility and an Attractive Target for Male Contraception. *Biol. Reprod.* **2020**, *103*, 345-356.
[3] Noman, M. A. A.; Kyzer, J.; Chung, S. S. W.; Wolgemuth, D. J.; Georg, G. I. Retinoic Acid Receptor Antagonists for Male Contraception: Current Status. *Biol. Reprod.* **2020**, *103*, 390-399.

Current Trends and Future Opportunities in Chemical Risk Assessment

Juliane Hollender

Swiss Federal Institute of Aquatic Science and Technology & ETH Zürich, Switzerland

Synthetic chemicals are everywhere in our daily life and are also the building block of energy- and resource-efficient technologies. The European Chemical Strategy for Sustainability is aiming to strengthen research towards a toxic-free environment where chemicals are produced and used in a way that maximises their contribution to society. Nevertheless, the number and volume of synthetic chemicals used worldwide is still increasing. Chemicals with hazardous properties can cause a threat to human health and the environment, as well as impacting and amplifying planetary crises such as climate change, degradation of ecosystems and loss of biodiversity. The situation is challenging for chemical risk assessment, where usually only a few compounds are monitored and the connected risk is assessed. Early warning and efficient action systems for chemicals to monitor the drivers and impacts of chemical pollution and the effectiveness of chemicals regulation are needed. Chemical analytical tools like high resolution mass spectrometry combined with data sciences and hazard prediction open new opportunities to address combined exposure to chemical mixtures from different sources and over time. Next to the general framework and the way forward, in this presentation examples of extended target, suspect and non-target screening of chemicals with liquid chromatography coupled to high resolution mass spectrometry for environmental monitoring and for evaluation of mitigation measures such as advanced wastewater treatment are presented and linked to risk assessment.

Self-Assembly of Gold Nanoparticles toward Biodetection

Luis M. Liz-Marzán[a,b,c]

[a] CIC biomaGUNE, Paseo de Miramón 182, 20014 Donostia-San Sebastián, Spain; [b] Ikerbasque, 48013 Bilbao, Spain; [c] CIBER-BBN, Paseo de Miramón 182, 20014 Donostia-San Sebastián, Spain

Nanoplasmonics can be defined as the science studying the manipulation of light using materials of size much smaller than the radiation wavelength. This technology finds applications in various fields including sensing and diagnostics. An essential component of nanoplasmonics are the nanostructured materials, typically noble metals, which can very efficiently absorb and scatter light because of their ability to support coherent oscillations of free (conduction) electrons. Although the remarkable optical response of "finely divided" metals is well known since more than 150 years ago, the recent development of sophisticated characterization techniques and modeling methods has dramatically reactivated the field. An extremely important pillar supporting the development of nanoplasmonics has been the impressive advancement in fabrication methods, which provide us with an exquisite control over the composition and morphology of nanostructured metals. Colloid chemistry methods in particular have the advantages of simplicity and large-scale production, while offering a number of parameters that can be used as a handle to direct not only nanoparticle morphology but also surface properties and subsequent processing.

This talk will introduce fabrication methods that allow fine tuning of the morphology of nanoplasmonic building blocks, with the ultimate goal of improving their optical properties and their performance in sensing applications. Several examples will be presented in which nanostructured materials comprising gold nanoparticles were used as substrates for ultrasensitive detection of biorelevant molecules.

[1] G. Bodelón et al., *Nature Mater.* **2016**, *15*, 1203-1211.

[2] L.M. Liz-Marzán, M. Grzelczak, *Science* **2017**, *356*, 1120-1121.

[3] J. Kumar, H. Eraña, E. López-Martínez, N. Claes, V.F. Martín, D.M. Solís, S. Bals, A.L. Cortajarena, J. Castilla, L.M. Liz-Marzán, *PNAS* **2018**, *115*, 3225-3230.

[4] J. Plou, M. Charconnet, I. García, J. Calvo, L.M. Liz-Marzán, *ACS Nano* **2021**, DOI: 10.1021/acsnano.1c01878

Squalene-Based Nanocarriers for the Delivery of Small Molecules

Patrick Couvreur

University of Paris-Saclay, France

The “squalenoylation” is a technology that takes advantage of the squalene's dynamically folded molecular conformation, to link this natural and biocompatible lipid with drug molecules to achieve the spontaneous formation of nanoassemblies (100–300 nm) in water, without the aid of surfactants. It was observed that these squalene-based nanoparticles are using the circulating LDL as “indirect” carriers for providing long-circulating properties and targeting cancer cells with high expression of LDL receptors. The application of the “squalenoylation” concept for the treatment of brain ischemia and spinal cord injury will be discussed too. It was also discovered that the linkage of squalene to leu-enkephalin (a neuropeptide) (i) prevented rapid plasma degradation of the peptide, (ii) allowed to target the peptide into the body painful area, (iii) conferred to the targeted neuropeptide a significant anti-hyperalgesic effect, (iv) without the morphine side effects (ie. Addiction, tolerance and resiratory depression). Very recently, the construction of multidrug nanoparticles containing both adenosine-squalene and vitamin E, allowed to inhibit the pathological cross-talk between oxidative stress and inflammation, occurring in complex and multifactorial phenomenon of uncontrolled inflammation occurring also in Covid-19 infection.

Refining Hit Identification Approaches for Tough Targets

Mark C. Noe

Vice President at Pfizer Worldwide R&D, Groton, Connecticut, U.S.A.

It is estimated that the human pharmacopeia only covers 10% of the disease-related target landscape, offering tremendous potential for designing new medicines that transform the lives of patients. However, at least half of this untapped target space lies outside the realm of druggable protein targets. Regulating protein homeostasis through induced proximity is a rapidly growing field that offers promise for tackling these novel targets. However, use of chimeric small molecules for this purpose still requires a quality small molecule that binds to the protein of interest. This presentation will describe recent advances in affinity selection mass spectrometry (ASMS) and DNA encoded library (DEL) screening that enables the identification of quality small molecule binders to tough targets. These advances include optimization of separation time, achievement of high compound compression ratios and improved data analysis capabilities for ASMS, and on-DNA resynthesis coupled with bead-assisted lead identification for DEL. Several brief case studies will be presented from our internal experience at Pfizer.

.

Protochemistries -- Chemistry before there were Chemists

Roald Hoffmann

Cornell University, Ithaca, U.S.A.

People did chemistry, superb chemistry, before there were ever chemists. For transformations of matter are inherent in the human condition. In winning metals from their ores, using them in weapons and decorative objects, in preparing and preserving food, in cosmetics, medicines, ceramics, in tanning leather, in dyes, in cleansing and mummification, craftsmen and women in every culture came up with some superb experimental chemistry. These stories of protochemistry, some of which I will relate, to this day form a natural bridge between chemists and nonchemists , between chemistry and culture. They stress the essential importance of experiment, and… of the underlying economics that governs much human activity. Much more than local color, these stories tender homage to the past, to the ingenuity of human beings. Protochemistries also connect our world, in time and in substance; their stories normalize science. And they plant science firmly in the context of world culture – chemistry in culture, culture in chemistry.

Novel Chromatographic-Mass Spectrometric Procedures in Art and Archaeology

Maria Perla Colombini

Dipartimento di Chimica e Chimica Industriale, University of Pisa

Since ancient times, proteins, oils, plant gums, natural resins and resinous materials played a prominent role, since their intrinsic properties meant that they could be employed for a variety of uses, basically, as painting materials, adhesives, hydro-repellents, coating and sealing agents, but also as flavours, incense, ingredients for cosmetics, medicines and mummification balms. The chemical characterization of such organic materials when properly integrated with related information from historical sources and archaeological data, has in the last few years considerably improved our knowledge of painting techniques, crafts, and technologies of the past, and has provided archaeologists with valuable information. In fact, identifying specific materials from molecular patterns helps in assessing the role that these substances played and in determining the use of artefacts on which these residues survive. The chemistry of these system is challenging: natural substances are inherently difficult to characterize and degradation due to ageing and storage, and chemical changes due to human activities make their identification even more complicated.

The analytical procedures based on mass spectrometric techniques applied to objects able to identify artistic/archaeological materials and to study their degradation pathways are outlined. Analytical pyrolysis (EGA-MS and Py-GC/MS), and chromatography/mass spectrometry (GC-MS and HPLC-MS) will be discussed highlighting their abilities in solving complex molecular mixtures and in achieving reliable results. To overcome the problem of micro sampling, an innovative fast non-invasive approach based on transportable selected ion flow tube-mass spectrometry (SIFT-MS) to profile VOCs in situ is discussed. The most significant potentiality of the technique and results obtained by analysing the VOCs released in situ by Egyptian findings belonging to the famous tomb of Kha (New Kingdom, XVIII dynasty, 1425– 1353 BC) at the Egyptian Museum of Turin (Italy) are herein presented.

The Beauty of Chemistry

Yan Liang

University of Science and Technology of China (USTC); Beauty of Science

For chemists, most would say chemistry is beautiful: they found its beauty in the magical transformation of matters, or in the countless arrangement of atoms forming all the useful molecules and materials such as medicines and semiconductors that are at the foundation of our modern world. For the public, however, things could not be more opposite: many will not realize the importance of chemistry as it always lies in the background of everyday life, or some might say chemistry is boring as they had terrible experience in learning chemistry in middle or high schools.

In this talk, the speaker will share his personal experiences of discovering the beauty of chemistry and sharing the beauty with the public by blending science and art through online videos, comics and animes, books, and digital learning resources for K-12 education. The speaker hopes this talk could inspire young chemists to pursue future careers in science communication and education, bringing the beauty of chemistry to more people.

Enzymes as functional models for the design of solid catalyst: From the model to the industrial application

Avelino Corma

ITQ-UPV-CSIC

Catalysis has been a key discipline for the advances in chemistry. In the case of heterogeneous catalysis great industrial advances have been achieve in the last seventy years. Most of those have been realised on the bases of accumulated knowledge, intuition, trial and error and good chemical science. It is not uncommon that in a number of those processes the applications have gone beyond the fundamental knowledge existing in that time. Even more, the industrial results have been feeding the development of fundamental knowledge.

In our presentation will show one way to go from the fundamental knowledge into the industrial application. Then, for developing solid catalyst, we have used as a functional model the natural catalyst, enzymes. Following this model, we have studied the catalytic mechanism to rationalise the nature of the active sites for a given catalytic reaction. We have developed bottom-up synthesis methodologies to introduce well defined single or multiple sites, while exploring the structural capabilities of the solids to select by molecular confinement and weak interactions, one reaction pathway when two or more are competing. We will show that in most cases solid catalyst requires higher reaction temperatures than enzymes and then entropic factors may have an important impact on the activation energy to achieve the desired transition state, and we will present the relevance of the short and long range interaction to stabilize the desired transition state. We will attempt to demonstrate how the combination of advanced synthesis methods, in situ and operando characterisation of materials, kinetic studies and molecular modelling can be determinant for designing those catalysts with well defined single or multiple isolated sites and achieving confinement effect.

Following this methodology, it is possible to design solid catalyst with high activity and selectivity by confining active sites into hybrid and inorganic mesoporous and microporous structured solids, that will allow us to go from the molecular design up to the industrial application of our solid catalysts. This methodology it is valid for carrying out multi-step processes in cascade mode using purely inorganic or hybrid multisite structures, by combining different solid catalysts, or by combining solid catalysts and enzymes.

Chemistry for a Sustainable Development

Lidia Armelao

Dipartimento di Scienze Chimiche e Tecnologie dei Materiali, Consiglio Nazionale delle Ricerche, Roma
Dipartimento di Scienze Chimiche, Università degli Studi di Padova

Chemistry must engage as one of the key forces that can identify and implement solutions to avert or mitigate potential crises and provide sustainable processes and products for the future. As the basis of a wide range of technologies, in combination with the well-established capacities for innovation, the chemical sciences are central to the development of clean and sustainable forms of energy, for example, through efficient capture of solar energy, clean fuel cells and carbon capture, storage and reuse, to the application of green chemistry principles and processes to manufacturing and for materials substitution, to ensuring the efficient and affordable recycling of resources in short supply including endangered elements and natural products, and to developing new analytical techniques suitable for more effective monitoring of the environment. [1,2,3]

This presentation aims at giving an overview of the challenges and opportunities that are connected with the ecological transition, offering some examples on how chemistry can play a key role for radical changes in different areas ranging from clean energy to sustainable production, and rational use of materials. Some examples of the forefront research activities conducted in these areas at the Department of Chemical Sciences and Materials Technologies (DSCTM CNR) will be highlighted.

[1] S. A. Matlin, G. Mehta, H. Hopf, A. Krief "The role of chemistry in inventing a sustainable future" Nature Chemistry 7, 941–943 (2015).
[2] T. Keijer, V. Bakker, J. C. Slootweg "Circular chemistry to enable a circular economy" Nature Chemistry 11, 190–195 (2019).
[3] J. B. Zimmerman, P.T. Anastas, H. C. Erythropel, W. Leitner "Designing for a green chemistry future" Science 367, 397–400 (2020)

From Waste to Resource: Issues and Innovative Sustainable Solutions

Mario Marchionna

Saipem SpA

Embracing new models that create value and safeguard the environment by improving the management of resources, eliminating waste through a better design, and maximizing the circulation of the products is one of the pillars of our strategy towards a more and more extensive decarbonization.
Technology is a key enabler to all four elements of Circular Economy - i.e. reduce, reuse, recycle, and remove - and the development of innovative solutions to sustainably treat any kind of waste produced by urban, commercial, and industrial activities (Oil & Gas, Petrochemistry, Cement, Iron & Steel, Pulp and Paper, …), with their consequent valorization to energy and/or valuable products, is becoming an important asset.

Confining our interest to plastic recycling, disposal and recycle of plastic wastes are key topics for which a comprehensive solution needs to be found and developed soon. A potential new, important market is growing but many challenges need to be faced.

As a major international contractor, we have started the analysis, planning and implementation of plastic recycling projects, with the business vision that the industry is developing. As a result, the main challenges gradually emerging from the project works become clear and their analysis can help tuning the overall vision. Several and very diverse stakeholders are involved (plastic producers, waste sorters and transporters, municipalities, …), and it is important to realize the contribution expected from every of them as well as the state of the art of this developing business with its different possible operating models. There is no “one-solution-fits-all” approach and there is a great need for players who can have a holistic, high-level vision to the problem while maintaining the capability to implement specific projects tailored to regional situations with unique operating and financial constraints.

As an ambitious final target, we could imagine a modular facility bringing together different technologies to treat all type of plastics in one location to its most suitable treatment, to produce new plastic, chemicals, power, and steam to ensure the circularity of plastics. The facility will seek the highest energy efficiency possible and will capture CO_2.

In the above contest, we are developing different technology options, in order to develop different solutions to be flexibly deployed according to the specific situations. Among them we may mention: clean combustion, with CO_2 recycle to urea or methanol production, through ITEA’s ISOTHERM Pwr® “Flameless” Oxy-Combustion [1], gasification to produce syn-gas to be possibly converted to chemicals - Saipem has an agreement with a technology provider in order to co-develop a pressurized gasification technology to produce syn gas from waste - and pyrolysis with product recycle to the Steam Cracker; in this respect Saipem has entered into an agreement with Corepla (national plastic recovery consortium) and Quantafuel to jointly promote circular economy models for plastic waste, and to seek building chemical recycling plants throughout Italy.

[1] M. Marchionna, *Oil & Gas Eur. Mag.* **2020**, *46 (2)*, 43.

Società Chimica Italiana

SCI2021

CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

- Orals
- Posters

Sars-CoV-2 airborne transmission: indoor and outdoor implications

G. de Gennaro[1], A. Di Gilio[1], J. Palmisani[1], L. Setti[2],F. Passarini[2], P. Barbieri[3], S. Licen[3], M.G. Perrone[4], A. Piazzalunga[5], M. Borelli[3], E. Rizzo[6], A. Colao[7], F. Cerino[8],M. Cacace[8], P. Piscitelli[9], A. Miani[10]

[1] Biology, University of Bari "aldo Moro", Bari, Puglia, Italy
[2]Industrial Chemistry "toso Montanari",
[3]Chemical and Pharmaceutical Sciences, University of Trieste, Trieste, Friuli-Venezia Giulia, Italy
[4]TCR TECORA, Milan, Italy
[5]Water and Life Lab, Bergamo, Italy
[6]Italian Society of Environmental Medicine, SIMA, Milan, Italy
[7]Medicina Clinica e Chirurgia, University of Naples Federico II, Napoli, Campania, Italy
[8]Befreest srl,viale Virgilio 113 - 74121 Taranto, Italy
[9]Euro Mediterranean Scientific Biomedical Institute, Bruxelles, Belgium
[10]Scienze e Politiche Ambientali, University of Milan, Milano, Lombardia, Italy

The COVID-19 pandemic due to the Severe Acute Respiratory Syndrome Coronavirus-2 (SARS-CoV-2) caused the shutdown of entire nations all over the world. To date, interdisciplinary approach-based scientific researches aim to deepen the factors underlying the transmission of SARS-CoV-2 in order to minimize its spread. The existing theories speculate on three main viral transmission pathways: a) transmission by exhaled droplets; b) airborne transmission by virus-containing aerosol and c) transmission via fomites through the direct contact with contaminated surfaces[1]. The viral transmission via virus-laden droplets is a well-established transmission pathway based on the transfer of larger respiratory droplets (with diameter ranging from 5 to 20 µm) from one infected subject to other subjects at close proximity through coughing, sneezing or speaking. Instead, the significance of the airborne transmission of SARS-CoV-2 through the exhalation of small microdroplets (also commonly referred to as ‘aerosols’) has been the object of an extensive discussion within the International scientific community. Several studies have shown that the airborne transmission route could spread some viruses over a distance of 2 meters from an infected person. In fact, researchers all over the world have proved the higher aerosol and surface stability of SARS-COV-2 as compared with SARS-COV-1 (with the virus remaining viable and infectious in aerosol for hours) and that airborne transmission of SARS-CoV can occur besides close-distance contacts[2].

In order to deepen this point, in this study the association between the mortality rates due to COVID-19 as well as the number of the confirmed new cases and the average concentrations of PM10 exceeding a daily limit of 50 µg/m^3 was investigated for Italy. Exceedance of the daily limit value of PM10 appeared to be a useful predictor of infection in univariate analyses ($p<0.001$). In fact, a significant association was found between the geographical distribution of daily PM10 exceedances and the initial spreading of COVID-19 in the 110 Italian provinces [3].

In addition, a pilot study of surveillance activity based on real time monitoring of CO_2 levels was conducted inside several Italian schools during the reopening among the lockdown periods due to COVID-19 pandemic in order to: a) explore the potential SARS-CoV-2 transmission risk, b) investigate the possible transmission route and factors influencing its and c) promote the safe reopening of schools. The indoor CO_2 monitoring was proven to be a practical proxy of the transmission risk of respiratory infectious disease.

References

[1]WHO Regional, 2000. Air Quality Guidelines for Europe Second Edition. https://www.euro.who.int/__data/assets/pdf_file/0005/74732/E71922.pdf
[2] Van Doremalen, et al., 2020. N. Engl. J. Med. 2020, 382, 1564–1567.
[3] Setti et al., 2020. Intern. J.of Environ. Res.and Pub. Health 17, 2932. https://doi.org/10.3390/ijerph17082932

Silk and sanitizing solutions: the need to protect visitor and artworks

B. Favaro[a], E. Balliana[a], F.C. Izzo[a], L. Falchi[a], P Lucero-Gomez[a], D. Cimino[a], E. Zendri[a]

[a] *Deprtament of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Venice*

The ongoing Coronavirus crisis involved almost all sectors as well as museums, collections, and historical sites all over the world. The pandemic officially introduced in cultural sites alcohol-based products (even by visitors for personal use) as these products have been indicated to inactivate the virus and were imposed by many local authorities [1]. In this context, the need to conciliate the safety of the visitors and the protection of artworks represents a challenging task. A risk for artworks due to the accumulation of vapour, as a consequence of ordinary room sanitization, or the contact with accidental spill of products, potentially caused by visitors, is of concern and should be evaluated. Artworks are in fact not always conserved in glass case or museums and the possibility that accidental contact can occur are not so far from possible in particular in historical buildings used as museum. In this case, the building itself has to be considered the artwork despite what it is conserved within its walls.

The present research reflects specifically on the possible interactions between sanitizing alcohol-based products and silk. Silk is a fragile and important materials well diffused in many cultural sites, such as historical buildings, museums and churches in Venice, all over the world on upholsteries and tapestries. The sanitising solution (75% ethanol, 20% water, 5% benzalkonium chloride BZK) selected by the Italian Ministry for Cultural Heritage (MIBACT) was here considered as the reference products for the tests [2]. Fours silk fabrics, different for production, age and aspects, were considered and subjected to vapour exposure for 10 days and immersion tests (30min and 24h) with the MIBACT solution. Pure distilled water, absolute ethanol and water/ethanol blends in different concentrations were also tested to evaluate possible influence and impact of each compound. Chemical and morphological variations on the silk have been evaluated with Scanning Electron Microscopy - SEM, Atomic Force Microscopy - AFM and portable instruments (contact microscope, colorimeter, Infrared and Raman spectroscopy). IR and Raman analyses did not detect significant chemical changes in the silk fabrics [3,4]. However, Raman spectra showed, after immersion treatments, minor variations in the intensity of peaks attributed to dyes. Vapour test, developed in these experimental conditions, did not give relevant spectroscopic changes; nevertheless, colourimetric variation could be observed. The consistent colour variations of the coloured silks, observed after immersion treatments, were mainly caused by ethanol/water blend within a concentration range of 70%-79% and were only partially influenced by the presence of BZK. Residues of BZK after immersion tests in sanitising solution are present, confirmed also by SEM and AFM analyses.

This research highlighted no evident morphological and chemical modifications related to the use of sanitizing solutions on silk but showed other drawbacks such as colour modification, equally important when referring to cultural objects. A change in colour, as showed by this study, especially if limited to a spot or a partial area, would represent a detrimental effect. Even though BZK reduces material surface tension and has antimicrobic action, can deposit on fiber affecting their micro-structure.

[1] K. Toshiyuki, O. Adetunji, P. Jurčys, S. Niar, J. Okahashi, V. Rush, 2020. http://openarchive.icomos.org/id/eprint/2415.

[2] MIBACT 2020, https://bce.chiesacattolica.it/wp-content/uploads/sites/25/MIBACT-SABAP-RM-MET_UO2-07-05-2020-0009719-P.pdf -19

[3] M.A. Koperska, D. Pawcenis, J. Bagniuk, M.M. Zaitz, M. Missori, T. Łojewski, J. Łojewska, *Polym. Degrad. Stab.* **2014**, *105*, 185

[4] D.S. Dwyer, R.J. Bradley, *Cell. Mol. Life Sci.* **2000**, 57, 265.

Combining the highest degradation efficiency with the lowest environmental impact in zinc oxide based photocatalytic systems

Mattia Costamagna[a], Luca Ciacci[b,c], Maria Cristina Paganini[a], Paola Calza[a], Fabrizio Passarini[b,c]

[a]Department of Chemistry, University of Turin, Via P. Giuria 7, 10125, Torino, Italy; [b]Department of Industrial Chemistry "Toso Montanari", University of Bologna – Alma Mater Studiorum; [c] Interdepartmental Centre for Industrial Research – Renewable Resources, Environment, Sea and Energy – University of Bologna – Alma Mater Studiorum

Augmenting and improving access to water sources is one of the most urgent priorities to address in the coming years for the achievement of the sustainable development. In this view, advanced oxidation processes such as heterogeneous photocatalysis are promising means to pursue efficient pollutants removal from unconventional water sources such as wastewater streams. However, energy requirements in the production of photocatalytic systems as well as in the degradation process may affect the overall environmental performance of the system so that a quantitative assessment of the process efficiency and the associated environmental implications is essential to the setting of strategies for long-term sustainability.

In this study, the photocatalytic degradation of phenol in a water stream was investigated by means of a combination of design of experiments (DoE) and life cycle assessment (LCA) techniques with the goal of identifying the best operating conditions that combine the highest degradation efficiency with the lowest environmental impact [1]. Based on previous works of the authors [2], zinc oxide doped with rare earth elements was the photocatalytic system considered for phenol degradation. The DoE experimental plan included as the model parameters the photocatalyst concentration, the type of rare earths used as a dopant (i.e., CE, Er, and Yb), its production route (i.e., from chloride or from nitrate precursors) and the dopant content in the photocatalytic system. A DoE face centered design was modeled to capture both linear and quadratic terms of the variables as well as their interaction effects on the degradation rate. LCA was then combined to the DoE results to evaluate the overall environmental performance of each photocatalysis scenario. Energy consumptions and irradiation time to complete photodegradation were directly measured from laboratory experiments, while complementary life cycle inventories were gathered from datasets reported in the literature and the Ecoinvent database. Life cycle impact assessment was carried out for the cumulative energy demand (CED) and the IPCC 2013 global warming potential (GWP) 100y methods.

The DoE results enabled to explore the full spectrum of degradation rates at all the combinations of the operation conditions. Compared to bare zinc oxide photocatalyst, the higher the dopant concentration, the faster the photocatalysis, with the overall preference following the order Ce > Yb > Er. However, a higher content of the dopant implies an increase of the environmental impacts, which is more relevant for rare earth production than for other metals [3]. Therefore, while the results show the highest degradation efficiency at 1700 mgL-1 of zinc oxide doped with Ce from nitrate, setting the photocatalytic system at 800 mgL-1 may be the preferable solution to reduce the environmental impact without compromising the degradation rate significantly. The DoE-LCA combined approach proposed in this work resulted to be particularly informative so that its application is highly recommended for quantitative analysis aimed at optimizing strategies for environmental protection and conservation.

[1] Costamagna et al., *J. Clean. Prod..* **2020**, *252*, 119762.

[2] Calza et al., *J. Hazard. Mater.*, **2017**, *323*, 471-477.

[3] Ciacci et al., *Resour. Conserv. Recy.*, **2019**, *142*, 143-152.

PROCRAFT project: conservation strategies of aircraft heritage from excavation to museum

Andrea Balbo[a], Elena Bernardi[b], Magali Brunet[c], Cristina Chiavari[b], Christophe Deshayes[c], Jane Echinard[e], Jaromir Fiser[d], Carla Martini[b], Cecilia Monticelli[a], Luc Robbiola[c], Cecilia Velino[b], Tomaš Vyhlidal[d], Elodie Guilminot[e]

[a]University of Ferrara, Italy; [b]University of Bologna, Italy; [c]CEMES, CNRS, Université de Toulouse, France; [d]Czech Technical University in Prague, Czech Republic; [e]GPLA-Arc'Antique, Département de Loire Atlantique, France.

Historical aircraft, especially those dated from Second World War (WW2), which is considered as the "golden age" of military aviation, have only recently entered the field of archaeology and cultural heritage conservation, and only a few are exposed in national museums. Actually, a wide number of these aircrafts is underground, in the European soils and seas. The care of these remains, which have an undeniable and emotional value for Europeans, is mainly taken by volunteers and associations. Hence, the development of innovative solutions for the conservation and the protection of these wrecks is the goal of the PROCRAFT JPI-CH project, which connects several partners across the Europe. The project is structured in several work packages, concerning the study of original remains, the development of suitable coatings, accelerated ageing tests on coated materials, and studies on reference sites. Firstly, the WW2 aircraft or wrecks were identified and recorded following the work carried out by associations on remains collected from six different nations: Germany, France, Italy, USA, UK, and USSR. The classification of each piece contained detailed information on the historical content, the circumstances of the crash and the overall conditions at the time of the discovery. Secondly, the constituent materials of the wrecks (aluminum alloys and protective coatings) were identified in laboratory through macro and microscale observations coupled with elemental and structural analyses, which allowed to determine the exact composition of the alloy as well as the nature of the original coatings. The analyses carried out on the wrecks gave an extensive overview of the type of alloys used in different countries in the last century. Two alloys, Duralumin and Super Duralumin (with a higher content of Mg) were employed for structural and non-structural parts. Moreover, due to the different strategies applied by the constructors (cladding, anodization, or deposition of an anticorrosion primer), the structural alloys were subjected to a large panel of alterations, amongst which pitting, exfoliation or galvanic corrosion. Recording and analyzing the degradation state of the artifacts aimed not only to valorize this part of aeronautical heritage, but also to determine and understand the parameters driving the aluminum corrosion in order to adapt its restoration treatments and find an appropriate protective coating for the material.
Preliminary results on Italian wreck rests characterization are here reported.

Airborne microplastics over the Baltic: influence of sea emissions

L. Ferrero[1], L. Scibetta[1], P. Markuszewski[2,3,4], M. Mazurkiewicz[2], V. Drozdowska[2], P. Makuch[2], E. D. Nilsson[3,4], P. Jutrzenka-Trzebiatowska[5], A. Zaleska-Medynska[5], Sergio Andò[1,6], Francesco Saliu[1], N. Losi[1], A.M. Cefalì[1], A. Bigogno[1], E. Bolzacchini[1]
[1]GEMMA and POLARIS Centre, University of Milano-Bicocca, 20126 Milano, Italy
[2]Institute of Oceanology, Polish Academy of Sciences, 81-712 Sopot, Poland
[3]Department of Environmental Science, Stockholm University, Stockholm, Sweden
[4]Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden
[5]University of Gdansk
[6]Laboratory for PROVENANCE Studies, DISAT, University of Milano-Bicocca, 20126 Milano, Italy

Plastic and microplastics (MP) pollution is one of the major problem of contamination on Earth as a whole connected environment. MPs have been found in all-natural environments and recently, even in the atmosphere [1-4]. In particular, this study addresses the interaction between microplastics and sea spray. The huge amount of microplastics in the sea might be released in the air via marine spray and bubble bursting. This latter, accounts for thousands of Tg y^{-1} of material in the atmosphere, supporting the aforementioned hypothesis.

To test this hypothesis the oceanographic survey was carried out in the Baltic sea using the Polish OCEANIA research vessel. During the cruise on the Baltic Sea, several samples have been collected using a Deposition Box capturing airborne particles on glass slides. Simultaneously sea MPs, have been sampled with a 300 µm mesh net. In addition, ancillary atmospheric parameters like black carbon (BC) concentrations (AE33 Aethalometer), aerosol number, aerosol size distribution (LAS and OPC measurements), sea spray fluxes, and meteorological data were available. Airborne microplastics (AMPs) were detected in all analyzed samples, indicating a ubiquitous prevalence of AMPs in atmospheric environments of the Baltic Sea marine boundary layer. Effectively, microplastics abundances (numbers of pieces per m^3) thus ranged from 0 to 682 m^{-3} with an average concentration of 139±74 m^{-3} (mean±95% confidence interval).

Its noteworthy that, despite the high concentrations, AMPs represented a negligible fraction concerning the total aerosol number concentration (from 90 nm up to 40 µm; LAS+OPC data): AMPs accounted only for $3.8*10^{-5}\pm2.0*10^{-5}$%.

Most of the samples were collected offshore where the influence of anthropogenic sources is minimal. Therefore, the presence of AMPs detected during that cruise may have originated from the marine spray that spread microplastics in the atmosphere triggered by the wind. Concentrations of marine microplastic (MMPs) ranged between 22 and 160 MMPs m^{-3}. At most stations blue/black fibers dominated (from 76 to 89%).

AMPs and MMPs have been analyzed using an inVia Renishaw µRaman spectrometer and all the spectra were collected using a 532 and 785 nm laser a 50x long working distance objective and a low laser-power intensity. Previously, it has been created an in-house library using the spectra of several industry and ambient plastics. In this respect, it was possible to catalogize various AMPs: flame retardant rubber (34%), polycarbonate (21%), polyethylene-polyethylene terephthalate (21%), polyurethane (10%), polyvinyl components (8%), Nylon (3%), other (3%).

In conclusion, MPs were detected in the marine atmospheric environment and atmosphere, showing a correlation ($R^2>0.9$) between the emission of sea spray and AMPs concentrations. Moreover, the vast majority of MMPs were PE, PP, PS, and nylon that are the most common plastic categories that can be found in the environment.

References

[1] González-Pleiter, et al., 2021. Science of the Total Environment 761, 143213. doi:10.1016/j.scitotenv.2020.143213
[2] Chen, G., Feng, Q., Wang, J., 2020. Science of the Total Environment 703, 135504. doi:10.1016/j.scitotenv.2019.135504
[3] Zhang, Y., et al. 2020. Earth-Science Reviews 203, 103118. doi:10.1016/j.earscirev.2020.103118

Aknowledgements: GEMMA and PROVENANCE center in the framework of Project Miur "Dipartimenti di Eccellenza 2018-2022".

An indoor air pollution evaluation of the *Quarto Stato* museum

A. Bigogno[a]*, A.M. Cefalì*[a]*, N. Losi*[a]*, L. Scibetta*[a]*, A. Galli*[b]*, M. Martini*[c]*, C. Rostagno*[d]*, L. Ferrero*[a] *and E. Bolzacchini*[a]

[a]*GEMMA and POLARIS research centres, University of Milano-Bicocca, Milano, 20126, Italy;* [b]*CNR – IBFM, Institute of molecular bioimaging and physiology, Segrate (MI), 20090, Italy;* [c]*Department of Materials Science, University of Milano-Bicocca, Milan, 20126, Italy;* [d]*Polo Museale Regionale della Lombardia - MiBACT, Milan, 20121, Italy*

Environmental conditions of cultural heritage (CH) are among the most crucial aspects to be considered when determining the location, planning the accessing procedures and preventive measures, especially in a reality of environmental global change. CH can be affected by atmospheric particles and gaseous pollutants both indoor and outdoor, particularly those works of art characterised by a precarious conservational state. In the present work the indoor air quality characterization of the Museo del Novecento (Milan), one of the most relevant Italian contemporary art museums, is reported. We focused on the investigation of the case of "*Quarto Stato*" by Pellizza da Volpedo, an oil-based painting on canvas (293 x 545 cm) stored behind a partially locked glass case in a not-filtered indoor reality. For this purpose, a specific experimental setting was employed allowing to perform continuous high-time resolution monitoring activity of the main pollutants. A combination of several instruments was employed during the summertime (April-September 2019; 1 min time res): 1) an aethalometer (7-λ), 2) a Scanning Mobility Particle Sizer, 3) an optical particle counter, 4) a real-time NO_x-O_3 detector, 5) a low volume sampler for the collection of the total suspended particles (TSP) on PTFE and quartz filters. For what concerns the three dimensional fractions of PMs inside the museum, the results highlighted a visitors effect on the variability of the trends: visitors act as a carrier for the PM and contribute to the resuspension of PM_{10}, in fact its concentration is higher than $PM_{2.5}$ during the opening hours of the museum. A comparison between the concentrations of PM_{10}, $PM_{2.5}$ and PM_1 detected inside and outside the painting case, highlighted an decrease of the fraction [PM_{10}] (from 18.9 to 10.5 μg/m^3): the case was proved to act as a filter barrier of the coarse fraction. Black Carbon is a component of the fine fraction of PMx, and it infiltrates beyond the protective case, with an average indoor concentration of 725 ng/m^3. On the other hand, the daily trend of the gaseous fraction represented by NO_x shows a higher concentration of NO_2 than NO: the photochemical oxidation reaction of NO with O_3 leads the formation of NO_2 (origin secondary). In fact, the concentrations of NO_2 inside the museum were higher than the outdoor ones (ARPA 'Milano-Pascal' station); quite the opposite, the indoor daily trend of O_3 (3.6 μg/m^3) is lower than outdoors. Moreover, a coupled ion chromatography system was used to characterize the ionic inorganic fraction (anions and cations) of TSP and total particles (TP) sampled directly from the painting surface. The comparization between the percentage of the ionic composition of PTS and PT showed a difference in SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+}. In fact, the PT represent an integral of several years, and sulphates and nitrates are present in the same way; quite the opposite, the high concentrations of sulphates in PTS reflect the spring-summer season of the sampling period. The Ca^{2+} ion shows a consistent presence in the PT (18%) attributable to physiological loss of $CaCO_3$ material from the museum walls or to the plaster preparation ($CaSO_4$) of the painting. The average ionic fraction is equal to 36.4% of the environmental PTS, in line with the outdoor inorganic composition and justifiable with the absence of an air filtration system. The chemical composition of the PT on the painting can determine different effects on the pictorial matrix. The passing of the main guidelines limits (ISCR 2008; ASHRAE 2019) by some of the investigated pollutants could represent a risk for the correct preservation of the work of art.

This work was supported by the project "MOBARTECH: technological, interactive and participatory mobile platform for the study, the conservation and enhancement of historical and artistic heritage" (Lombardy Region).

Grafting on metal oxide nanoparticles surface reduces the toxicity of catechols

Elena Badetti[a], *Eleonora Faraggiana*[a], *Andrea Brunelli*[a], *Judit Kalman*[b], *Cinzia Bettiol*[a], *Francesca Caterina Izzo*[a], *José Maria Navas*[b], *Antonio Marcomini*[a]

[a] *DAIS - Department of Environmental Sciences, Informatics and Statistics, University Ca' Foscari of Venice, Via Torino 155, 30170 Venice Mestre, Italy.* [b] *INIA - Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria, Crta. de la Coruña, km 7, 5, 28040 Madrid, Spain.*

Due to the extensive use of manufactured nanoparticles (NPs) and the growing concern about their potential impact upon the environment, the toxicity of these materials has been widely investigated during the last years [1]. However, few studies reported how the interactions between NPs and aquatic pollutants may influence the toxic effects of the composite material that can be formed, as well as those of the individual components. In this study, the interaction between metal oxide NPs (TiO_2 and Fe_2O_3 NPs) and differently substituted catechols was investigated, by exploring different experimental conditions to increase the coverage of organic molecules grafted on the NPs surface.
Multiple analytical techniques were used to carry out an extensive physico-chemical and colloidal characterization of both pristine and functionalized metal oxide NPs, and three cytotoxicity assays (AlamarBlue, CFDA-AM, and Neutral Red Uptake) with the topminnow fish hepatoma cell line PLHC-1 were performed to assess the aquatic toxicity of all the materials and chemicals investigated [2]. The results showed cytotoxicity only for catechol's molecules, while both pristine and functionalized metal oxide NPs did not cause any toxic effect. These findings indicate that the grafting of catechols on the NPs surface, occurring through the hydroxyl groups [3], inhibited the cytotoxicity of all catechol molecules, suggesting a potential application of TiO_2 and Fe_2O_3 NPs to reduce phenol type pollutants' toxicity.

[1] S.J. Klaine, A. A. Koelmans, N. Horne, S. Carley, R.D. Handy, L. Kapustka, B. Nowack, F. von der Kammer, *Env. Tox. Chem.*, **2012**, *31*, 3.
[2] A. Bermejo-Nogales, M. Connolly, P. Rosenkranz, M.-L. Fernández-Cruz, J.M. Navas, *Ecotoxicol. Environ. Saf.*, **2017**, *138*, 309.
[3] A. Brunelli, E. Badetti, G. Basei, F.C. Izzo, D. Hristozov, A. Marcomini, *NanoImpact* **2018**, *9*, 114.

The new shades of the XX century: investigation of ACNA dyes through Raman spectroscopy and HPLC-MS

Alessandro Ciccola[a], *Ilaria Serafini*[a], *Flaminia Vincenti*[a,b], *Kathryn Raeburn McClure*[a], *Camilla Montesano*[a], *Manuel Sergi*[c], *Gabriele Favero*[d], *Paolo Postorino*[e], *Roberta Curini*[a]

[a] *Dept. of Chemistry,* [b] *Dept. of Public Health and Infectious Disease,* [d] *Dept. of Chemistry and Technology of drugs,* e) *Dept. of Physics, Sapienza University of Rome, Italy;* c) *Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Italy*

Since the unintentional development of mauveine (by British chemist Henry William Perkin) [1], both the manufacturing industry and the art world underwent a new phase of experimentation and development. Related objects from this period are hence very useful in the study of the history of manufacture, fashion, and contemporary art. Cultural heritage studies focussing on synthetic dyes represent a relatively new area of study due to their modernity, and research into synthetic textile dyes is becoming increasingly important[2–4]. A fulfilling comprehension of the early production and use of synthetic dyes can help to shape our understanding of these interesting periods of change in human behaviour, so the characterization of synthetic dyes in complex matrices of artistic and historical interest represents a breakthrough and a challenge in research for the conservation of Cultural Heritage.

In this work, a first step in understanding a full collection of synthetic dyes, held by the Museum of Chemistry of Sapienza University of Rome, is marked, providing insight into the composition of dyes produced by the Azienda Coloranti Nazionali e Affini (ACNA) in the first decades of XXth Century. A multidisciplinary protocol, based on the combination of Raman spectroscopy and High Performance Liquid Chromatography coupled to Mass Spectrometry, was applied for the complete characterization of the dyes; moreover, a specific clean-up procedure, adopted from food analytics[5], was adapted for the characterization of these analytes in textile matrices.

This study represents an excellent opportunity to understand the behaviours and synthetic procedures of a company that was active throughout the entirety of the 20th century, providing insight into the internal testing and motivations related to its market choices and resulting in a synthetic dye database useful for futher studies.

[1] W.H. Perkin, *J. Chem. Soc. Trans*. **1879**, *35,* 717.

[2] I. Serafini, L. Lombardi, C. Fasolato, M. Sergi, F. Di Ottavio, F. Sciubba, C. Montesano, M. Guiso, R. Costanza, L. Nucci, R. Curini, P. Postorino, M. Bruno, A. Bianco, *Nat. Prod. Res.* **2017**, 6419.

[3] I. Degano, E. Ribechini, F. Modugno, M.P. Colombini, *Appl. Spectrosc. Rev.* **2009**, *44*, 363.

[4] C. Souto, *Analysis of Early Synthetic Dyes with HPLC-DAD-MS: An important database for analysis of colorants used in cultural heritage*, Universidade Nova de Lisboa, **2010**.

[5] M. Faraji, B.N. Sahneh, R. Javanshir, *Anal. Bioanal. Chem. Res.* 2017, *4*, 213.

In Situ Electrochemical Oxidation for Destructive Treatment of PFAS

Angelo Fenti[a,b], *Andrea Hanson*[a], *Yukun Jin*[c], *Graham Peaslee*[c], *Shaily Mahendra*[d], *Pasquale Iovino*[e], *Jens Blotevogel*[a]

[a] *Dept. of Civil and Environmental Engineering, Colorado State University, Fort Collins, CO 80523, jens.blotevogel@colostate.edu;* [b] *Department of Engineering, University of Campania "Luigi Vanvitelli", 81031 Aversa, Caserta, Italy, angelo.fenti@unicampania.it;* [c] *Department of Physics, University of Notre Dame, Notre Dame, IN 46556, gpeaslee@nd.edu;* [d] *Dept. of Civil and Environmental Engineering, UCLA, Los Angeles, CA 90095, mahendra@seas.ucla.edu;* [e] *Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, University of Campania "Luigi Vanvitelli", via Vivaldi 43, Caserta, Italy, pasquale.iovino@unicampania.it*

Per- and polyfluoroalkyl substances (PFAS) have become a growing concern around the world due to their high persistence and resistance to natural and conventional degradation mechanisms. A few advanced treatment processes have been shown to break the strong carbon-fluorine bond and thus destroy PFAS, but their implementation remains a challenge. Among them, electrochemical oxidation is an emerging technology capable of mineralizing even the most persistent water contaminants such as PFAS. In this project, we are developing electrochemical oxidation treatment of perfluorooctane sulfonate (PFOS) carried out in a flow-through mesh electrode reactor. Mesh electrodes can be installed in a trench for in situ groundwater treatment as an electrochemically active barrier, thus were implemented here for bench-scale testing. Ti/IrO_2-Ta_2O_5 and Magnéli-phase Ti_nO_{2n-1} were used as cathode and anode, respectively. The impact of several process parameters on the electric energy per order (EEO) and anodic surface area per order (ASAO) of contaminant removed were assessed, including current density, electrolyte concentration, seepage velocity, and PFOS concentration (Figure 1.a). In operating the mesh reactor in recirculation mode, the results showed that 99.7% of PFOS degradation was achieved after 74 h of treatment time (Figure 1.b). Approximately 77% of the fluorine in PFOS was recovered as aqueous fluoride, indicating the cleavage of the carbon-fluorine bond had occurred as a result of electrochemical oxidation. While no fluorinated intermediates were detected in the aqueous phase, particle-induced gamma-ray emission (PIGE) analyses revealed the presence of fluorine intermediates in the gas phase. Our results demonstrate that electrochemical oxidation shows promise for in situ applications of PFAS destruction in groundwater.

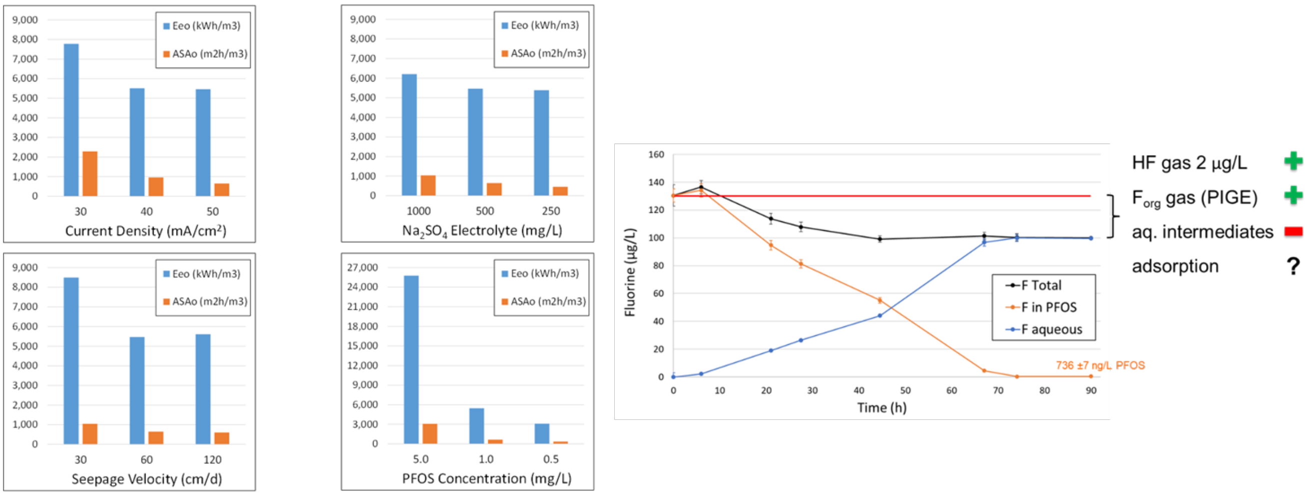


Figure 1. (a) Impacts of current density, electrolyte concentration, seepage velocity, and PFOS concentration on energy consumption (E_{EO}) and required anode surface area (ASA_O). **(b)** Fluorine mass balance for the electrochemical oxidation of PFOS in a recirculating mesh electrode flow-through reactor: PFOS concentration = 200 µg L^{-1}, Na_2SO_4 = 500 mg L^{-1}, NaCl = 10 mg L^{-1}, current density = 50 mA/cm^2, seepage velocity = 120 cm/d. The red line indicates total fluorine in the system at the start of the experiment.

Data fusion techniques based on Self-Organizing Map algorithm for the integration of different source/frequency instrumental data and ancillary information for environmental impact assessment

Sabina Licen[a], *Sergio Cozzutto*[b], *Gianpiero Barbieri*[b], *Aleksander Astel*[c], *Pierluigi Barbieri*[a]

[a] *Dept. of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1,34127 Trieste , Italy;* [b] *ARCO SolutionS s.r.l., spin-off company of the Dept. of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127 Trieste , Italy;* [c]*Department of Environmental Chemistry, Pomeranian University in Słupsk, ul. Arciszewskiego 22b, 76-200, Słupsk, Poland*

In the assessment for decision support of complex or poorly defined problems the use of heterogeneous data and information helps in the characterization of the object or process under study [1]. Approaches have been developed to consider jointly data produced by several instruments as well as qualitative data collected by human assessors [2]. In principle environmental monitoring in industrial areas with multiple non-stationary pollution emission sources allow collection of time series in which pollutants concentration data have highly irregular sequences, related to the several anthropic and natural processes impacting on measured parameters. Different data fusion approaches have been reviewed in papers and books and the approach proposed by the Data Fusion Group of the Joint Directors of Laboratories [3] has wide recognition. The JDL approach considers five levels of data fusion as follow: level 0-source preprocessing; level 1-object refinement; level 2-situation assessment; level 3-impact assessment; level 4-process refinement.

In the present study we show how the unsupervised modelling procedure based on the Self Organizing Maps introduced by Teuvo Kohonen [4], can be applied as JDL scheme for data fusion at several levels; the approach is exemplified with a case study on air quality assessment at an urban-industrial site. In particular we will introduce a criterium for the SOM model update, that correspond to level 4 (process refinement) in the JDL data fusion approach.

The afore mentioned approach has been applied to electronic nose and optical particle counter data together with meteorological, pollutants and subjective information (citizen complaints). The data has been recorded near dwellings in proximity of an industrial plant [5,6]. Starting from more than 100'000 vectors-per-minute (accounting for an overall number of single data of above 3 million) we obtained a reduced number of recurrent air type profiles (approx. 1'000) that could be classified in three clusters using k-means clustering algorithm applied to SOM outcomes. They have been characterized as "low impact", "medium impact", "high impact" observing the variable profiles in the clusters as well as linking the ancillary data (odor concentrations, pollutant data, citizen complaints records) to the clusters.

The data have been mined using a recently published tool, SOMEnv, a package with a Graphical User Interface that works in R software environment and has several built-in visualization features for high frequency data [7].

[1] F. Mureddu, J. Schmeling, E. Kanellou, *Transform. Gov. People, Process Policy*. **2020,** 14, 593

[2] S.A. Kashinath, S.A. Mostafa, A. Mustapha, H. Mahdin, D. Lim, M.A. Mahmoud, M.A. Mohammed, B.A.S. Al-Rimy, M.F.M. Fudzee, T.J. Yang, , *IEEE Access*. **2021,** 9, 51258

[3] F. Castanedo, *Sci. World J.* **2013**, 2013

[4] T. Kohonen, Self-Organizing Maps, *Springer series in Information Sciences*, **2001**.

[5] S. Licen, G. Barbieri, A. Fabbris, S.C. Briguglio, A. Pillon, F. Stel, P. Barbieri, *Sensors Actuators, B Chem.* **2018,** 263, 476

[6] S. Licen, S. Cozzutto, G. Barbieri, M. Crosera, G. Adami, P. Barbieri, *Chemom. Intell. Lab. Syst.* **2019**, 190, 48

[7] S. Licen, M. Franzon, T. Rodani, P. Barbieri, *Microchem. J.* **2021,** 165, 106181

Insights into the oil paint polymeric network by Solid State NMR

Francesca Nardelli[a], *Francesca Martini*[a,b], *Celia Duce*[a], *Jacopo La Nasa*[a], *Judith Lee*[c], *Anna Lluvears-Tenorio*[a], *Bronwyn Ormsby*[c], *Ilaria Bonaduce*[a], *and Marco Geppi*[a,b]

[a]*Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, 56124, Pisa, Italy;* [b]*Centro per l'Integrazione della Strumentazione Scientifica dell'Università di Pisa (CISUP), Lungarno Pacinotti 43, 56126 Pisa, Italy;* [c]*Conservation Department, Tate, Millbank, London SW1P 4RG, United Kingdom*

Modern and contemporary oil paintings present several conservation issues, ascribable to the differences in the formulation of the paints and to different artistic practices compared to earlier works. Among them, water sensitivity represents one of the major concerns for modern oil painting preservation, as it prevents the use of traditional water-based methods for surface cleaning, which may cause unwanted damages to the artworks. Specifically, the process of curing seems to play a key role for the manifestation of water sensitivity in oil paintings. Upon curing, triglycerides progressively crosslink and form a solid elastic polymeric network, which traps and stabilizes the pigments. It has been hypothesized that if the formation of the polymeric film during curing does not occur properly, competitive oxidative pathways may become predominant[1]. In such a case, the cured paint would contain a less extended polymeric network along with polar oxidation by-products, whose presence might contribute to water sensitivity. Due to the complexity of the systems, the molecular details of the degradation phenomena are not yet fully understood. The situation is quite intricate also because the majority of analytical techniques give information only on the soluble fraction of the oil matrix. Conversely, characterization of the crosslinked fractions is significantly more challenging, if possible at all. However, a complete knowledge of the physico-chemical properties of the whole sample is necessary in order to propose reliable strategies for the conservation of modern and contemporary oil paintings.

In this context, Solid State Nuclear Magnetic Resonance (SSNMR) spectroscopy can provide a substantial contribution. Indeed, several SSNMR experiments can be exploited to selectively characterize regions of the sample displaying different molecular mobility, since they can be distinguished on the basis of specific different nuclear properties, without the requirement of preventive extraction procedures or chemical treatments.

In this study we explored the use of SSNMR spectroscopy to gain insights into the chemical composition of the organic fractions of model paint layers, which present different behaviours towards surface cleaning with water. The study demonstrates a relationship between the painting stability and the chemical structure of the polymeric network. In particular, it is demonstrated for the first time that a low degree of cross-linking in combination with a high degree of oxidation of the polymeric network render the oil paint layer sensitive to water.

[1] I. Bonaduce, C. Duce, A. Lluveras-Tenorio, J. Lee, B. Ormsby, A. Burnstock, K. J. Van Den Berg, *Acc. Chem. Res.* **2019**, *52*, 3397–3406.

Advances in analytical methodologies applied to cultural heritage: first application of DLLME to characterize dyes in ancient textiles

Ilaria Serafini[a], Flaminia Vincenti[a,b], Kathryn Raeburn McClure[a], Alessandro Ciccola[a], Camilla Montesano[a], Manuel Sergi[c], Gabriele Favero[d], Roberta Curini[a]

[a] Dept. of Chemistry, [b]Dept. of Public Health and Infectious Disease,[d)] Dep. of Chemistry and Drug Technologies, Sapienza University of Rome, Italy [c)] Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Italy

Scientific research applied to cultural heritage is a very challenging field and requires the use of innovative analytical solutions for very complex questions, such as those related to historical textiles and works of art. The most critical issue is the analysis of natural dyes, due to the generally complex mixture that compose the colour and the very small amount of available samples. In literature, new extraction methods have been developed with the aim of maximizing the information obtained with reduced quantity of available materials [1-2].

From this point, we propose a novel approach for the extraction of natural organic textile dyes from historical, archaeological, and artistic matrices developed by Sapienza Group of Analytical Chemistry applied to Cultural Heritage. It represents the first time in which a clean-up procedure has been applied to cultural heritage analyses.

The approach involves the recently developed ammonia extraction protocol [3,4] and employs an innovative Dispersive Liquid-Liquid Microextraction (DLLME) method for clean-up [5]. The research builds upon the recently discovered benefits of the ammonia-based extraction protocol for efficient extraction and preservation of the sensitive but informative glycosyl moieties present in some natural dyes [3]. However, the cited method employs a traditional liquid-liquid extraction and is therefore not well-suited to the very small amounts of material available for analysis in the field of cultural heritage. On the contrary, the addition of the DLLME clean-up step to this protocol represents a significant improvement; in fact, the DLLME – which has been used in synthetic food dye analysis or in forensic science [6, 7]– offers a highly tunable method to purify and pre-concentrate natural dye molecules. The combination of the mild ammonia-based extraction method and the novel DLLME protocol with high performance liquid chromatography coupled with mass spectrometry (HPLC-MS) analysis, provides a higher recovery of dye analytes than observed with the traditional LLE method and therefore a significant improvement in sensitivity. Alongside this, the DLLME protocol was much more precise and efficient to perform on several samples simultaneously, highlighting the great potential of this typology of extraction to solve the major issues in Cultural Heritage analytics.

[1] L. Troalen, A. Hulme, *Anal. Methods*, **2021**, *13*, 558
[2] I. Degano, J. La Nasa, *Top. Curr. Chem.*, **2017**, 263–290
[3] L. Lombardi, I. Serafini, M. Guiso, F. Sciubba, *Microchem. J.*, **2016**, 126, 373–380.
[4] I. Serafini, L. Lombardi, G. Vannutelli, C. Montesano, F. Sciubba, M. Guiso, R. Curini, A. Bianco, *Microchem. J.,* 2017, 134, 237–245
[5] M. Rezaee, Y. Assadi, M.R. Milani Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, J. Chromatogr. A, **2006**, 1116, 1-9
[6] M. Faraji, B. Nasiri Sahneh, R. Javanshir, *Anal. Bioanal. Chem. Res.*, **2017**, 4(2), 213-25.
[7] F. Vincenti, C. Montesano, L. Cellucci, A. Gregori, F. Fanti, D. Compagnone, R. Curini, M. Sergi*, J. Chromatogr. A,* **2019**, 1605, 360348
[8] F. Fanti, F. Vincenti, C. Montesano, M. Serafini, D. Compagnone, M. Sergi, *J. Pharm. Biomed. Anal.,* **2020**, 186, 113302

Caput Mortuum purple hematite pigment: Investigation of magnetic properties

Sawssen Slimani[1,2,] Elena Castagnotto[1,3], Federico Locardi[1], Laura Gaggero[3], Fabio Canepa[1] , Davide Peddis[1,2]Maurizio Ferretti[1].

[1]Università di Genova, Dipartimento di Chimica e Chimica Industriale, nM2-Lab, Via Dodecaneso 31, I-16146, Genova, Italy ; [2]CNR, Istituto di Struttrua della Materia, nM2-Lab, Monterotondo Scalo (Roma), 00015, Italy; [3]Department of Earth, Environment and Life Sciences, University of Genoa, Corso Europa 26, I-16132,Italy

Abstract

Hematite-based purple dye called Caput Mortuum has been often reported in the context of pigments of art history. Recently, different groups proposed it to be made of violet hematite (α-Fe_2O_3), with the possible presence of secondary phases such as kaolinite [Al2Si2O5(OH)4]. Although, α-Fe_2O_3 is the most stable form of iron oxide, it may have a highly variable magnetic properties which arise from an ordered structure of non-magnetic chemical and/or lattice defects, causing then an imbalance between the antiferromagnetically coupled sublattices. In this study, different Fe-rich compounds were selected as starting materials, investigation by careful morpho-structural and mainly magnetic characterization the possibility of a natural origin has initially been explored. X-Ray Diffraction (XRD), show Good crystallinity of the samples with an increase of particle size with annealing temperature (e.g., $<D_{XRD\text{-}ANH}>=33(1)$ nm and $<D_{XRD\text{-}ASH}>=59(7)$ nm). This is confirmed by Transmission Electron Microscopy (TEM), that also indicate a tendency to the particles to be agglomerated. DC magnetic measurements shows clear difference among natural and synthetic samples. Synthetic one shows canonical antiferromagnetic behavior, with a linear field dependence of the magnetization. In natural samples the antiferromagnetic component is superimposed to a weak ferromagnetic one[1,2] (presence of some uncompensated spins) due to some impurities (i.e. magnetite or maghemite).

[1] Moriya, T., Physical Review, **1960,**120 (1),91–98.
[2] Dvořák, V., Physica Status Solidi (B), **1971,** 46 (2),763–772.

Colloidal behavior of titanium dioxide nanoparticles in artificial and in Venice lagoon waters in the presence of standard or natural colloidal particles

Andrea Brunelli[a], Aurelio Giovanni Foscari Widmann Rezzonico[a], Gianpietro Basei[a,b], Gigliola Lusvardi[c], Cinzia Bettiol[a], Elena Semenzin[a], Antonio Marcomini[a], Elena Badetti[a]

[a]*DAIS - Department of Environmental Sciences, Informatics and Statistics, University Ca' Foscari of Venice, Via Torino 155, 30170 Venice Mestre, Italy.*
[b]*GreenDecision Srl, Via delle industrie 21/8, 30175 Venice, Italy.*
[c]*University of Modena and Reggio Emilia, Via Campi 103, Modena, Italy*

The interactions involving engineered nanoparticles (NPs) and natural colloids in surface waters are known to be key factors in driving the environmental fate and behavior of NPs. Experimental procedures aiming at mimicking as much as possible environmentally relevant conditions are therefore highly needed. In this context, the colloidal behavior of TiO_2 NPs has been investigated in both artificial waters, i.e. deionized water, artificial fresh and marine waters added with Suwannee River natural organic matter (SR-NOM), as well as in the Venice lagoon water, in the presence of both standard kaolinite and the more complex natural colloidal particles (NCPs). Statistical and data visualization tools were then combined to highlight potential pattern among the different systems tested, in particular a global stability index (I_G) was used to compare the colloidal behavior of the different dispersions.

According to the I_G values obtained, kaolinite resulted a good model for mimicking the colloidal behavior of natural colloids extracted from the sediment of the Venice lagoon. For the more complex kaolinite/TiO_2 NPs and NCPs/TiO_2 NPs multi-component dispersions, the behavior between kaolinite and NCPs slightly changed. Moreover, the I_G values obtained for all the multi-component dispersions tested in both artificial and natural salty waters were almost similar, highlighting that artificial marine water could be a good surrogate of the Venice lagoon water for colloidal stability studies on NPs. As far as SR-NOM added to the artificial waters to simulate the NOM already contained in the NCPs extracted, its two-fold role of stabilizing the kaolinite dispersion and of favoring the destabilization of the kaolinite/NPs mixture was observed, particularly in the presence of the high ionic strength of the artificial marine water.

Assessment of the Cytotoxicity of Metal oxide Nanoparticles on the Basis of Immediately Available Physical-Chemical Parameters.

Felice C. Simeone

[a] *CNR-ISTEC, Via Granarolo, 64- Faenza; felice.simeone@istec.cnr.it*

We illustrate how known adverse modes of action of nanoparticles arise from fundamental physical-chemical parameters that don't need any experimental quantification. We show that cytotoxicity of metal oxides in different types of in-vitro systems can be foreseen on the basis of the values of oxidation number (Z) and ionic potential (IP) of the metal cation, and surface reducibility (SR), and redox reactivity (RR) of the oxide. Importantly, the values of these fundamental physical-chemical parameters can be easily determined from the chemical formula of the nanoparticle with the help of a periodic table. Combining these parameters in a naïve Bayes classifier, a robust probabilistic model that can be run on a pocket calculator, makes it possible to determine the most probable level of toxicity of a nanoparticle given its composition.

Results indicate that the probability that nano-oxides exhibit very high cytotoxicity ($EC_{50} < 10^{-3}$ mol·L^{-1}) decreases with increasing oxidation number Z of the cation; high values of Z, however, may become unstable and activate adverse redox processes; in contrast, stable, redox-inert reducible oxides tend to be, probabilistically, less toxic than oxidizable ones.

The simplicity of the approach enables non-specialists to formulate hypotheses about the toxicity of nanoparticles. Details are described in https://www.doi.org/10.1039/c9en00785g.[1]

The approach is available to anyone through the Nanocommons link https://app.jaqpot.org/model/2XyMtChRiSfZ6UmKirhi.

[1] F.C. Simeone, Costa A. L.

"Assessment of cytotoxicity of metal oxide nanoparticles on the basis of fundamental physical–chemical parameters: a robust approach to grouping"

Environ. Sci.: Nano, **2019**,6, 3102-3112

The effect of a karst-fractured aquifer on wastewater quality: an UHPLC-HRMS study

C. De Ceglie, S. Murgolo, G. Bagnuolo, R. Ciannarella, G. Mascolo

CNR, Istituto di Ricerca Sulle Acque, Via F. De Blasio, 5 – 70132 Bari

The presence in wastewaters of contaminants (pharmaceuticals, endocrine disruptors, personal care products, pesticides, and various industrial compounds) not efficiently removed from conventional treatment plants (WWTPs) poses a threat to the environment and human health.

These organic micropollutants, in fact, have been detected in different aqueous compartments such as groundwater at concentrations ranging from ng/L to µg/L.

Groundwater is the most valuable natural water resource for human needs. The natural composition of groundwater is related to the physical and chemical characteristics of the rocks that host the groundwater, to the infiltration process through the vadose zone, and the flow of the groundwater [1].

This study investigated the environmental contamination of groundwater as a consequence of the discharge of treated wastewater into the soil. The investigation focused on a wastewater treatment plant located in an area fractured by karst in the Salento peninsula (Apulia, Italy).

In this perspective, water samples were collected at three sites (treated wastewater, infiltration trench, monitoring well) and the occurrence of contaminants of emerging concern was investigated using an analytical detection method based on an ultra-high pressure liquid chromatography interfaced with a high-resolution tandem mass spectrometer with a duospray ion source operated in electrospray ionization (ESI) positive mode.

A gradual reduction in the concentration of contaminants of emerging concern was observed across the profile of soil fissured by karst (Figure 1); in particular, personal care products and X-ray contrast media were the contaminants that showed the greatest decrease in concentration from the infiltration trench to the monitoring well, whereas the highest residual concentration was detected for anticonvulsants, followed by antimicrobials and antipsychotic drugs.

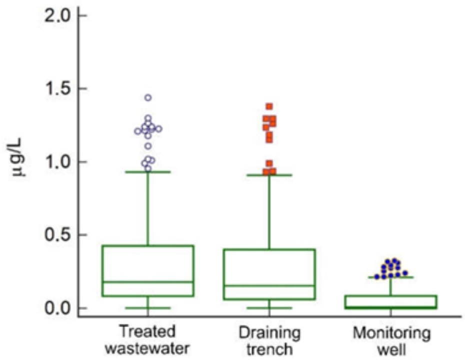


Figure 1. Distribution of the concentration values of the substances in the treated wastewater, infiltration trench and monitoring well.

Acknowledgment

This work was supported by Apulia Regional Government, Bari, Italy (DIEF 2018-19, prot. AOO_152/3459) within the Evaluation of Sanitary Risk Related to the Discharge of Wastewater to the Ground (SCA.Re.S) project.

[1] Y. Zhang, W.R. Kelly, S.V. Panno, W.T. Liu, *Sci. Total. Environ.* **2014**, *490*, 1082.

Plastic and its associated contaminants: determination of PAEs in coral reef invertebrates by *in vivo* SPME-LC-MS/MS

Francesco Saliu[a], *Simone Montano*[b], *Paolo Galli*[b], *Marina Lasagni*[a]

[a] *Earth and Environmental Science Department, University of Milano Bicocca, Piazza Della Scienza 1, 20123 Milano, Italy.*
[b] *MaRHE Center (Marine Research and High Education Center), Magoodhoo Island Faafu Atoll, Maldives*

The impacts of plastics and microplastics on marine life are currently under the spotlight. Several studies focus on the possibility that plastic particles may play a role as carriers of toxic contaminants into marine organism. Both plastic additives and environmental micropollutants adsorbed from seawater are part of the concern [1]. In the current literature, evidence that microplastics are ingested by marine organism and may transfer associated contaminants comes mainly from feeding experiments, that are carried out in captivity and by applying high dose exposures. Studies "on field" are limited because difficult to be arranged. Moreover, the detection of low concentration of microplastics and of plastic associated contaminants in marine organisms sampled from their "real environment" is challenging due to their presence as background in the common analytical laboratories. Finally, ethical limitations are posed when the surveys imply the use of sensitive or endangered species. To overcome all these issues, we developed new analytical procedures based on the application *in vivo* of solid phase micro extraction (SPME) coupled to liquid chromatography-tandem mass spectrometry (LC-MS/MS). Specifically, we optimized experimental condition for the extraction of phthalate esters (PAEs) and related metabolites. PAEs are common plastic "ingredients" blended with plastic polymers to enhance the flexibility of the plastic materials. Since they may be leached in the surrounding water, they are thus frequently researched as markers of plastic contamination, and in someway related to plastic ingestion, especially when detected in the tissue of filter feeders (2). By drawing extraction time curves in agarose gel aimed to mimic diffusion of PAEs from tissues to the extracting polymeric phase, we observed that 10 min of contact time of the fiber with the tissue is sufficient to extract detectable amount of the target analytes, this with an enhanced control of the procedural blank background contamination in respect to common solvent extraction approach. Moreover, thanks to an efficient sample clean-up the signal-to-noise ratio was determined an enhanced and balanced the low recovery related to the non-exhaustive nature of the microextraction procedure. Overall, these lead to substantial improvement of the limit of quantitation (LOQ's) and satisfactory performance in terms of sensitivity and repeatability. Finally, test *in vivo* on different marine invertebrates showed that the biocompatible material did not cause any temporary and macroscopicchange into the health status of the selected organisms.The method was therefore applied as replacement of lethal solvent extraction based approach for our current biomonitoring projects on coral reef environments. Some of the results of this surveys are here discussed.

[1] A. L Andrady, *Mar. Poll. Bul.* **2016**, *62*,1596

[2] M.C. Fossi et al., *Mar. Poll. Bul.* **2012**, *64*, 2374

[3] J. Pawliszyn, Solid-Phase Microextraction—Theory and Practice, Wiley-VCH, New York, 1997.

[4] F. Saliu, S. Montano, B.W. Hoeksema, M. Lasagni, P. Galli *Anal. Methods,* **2020**, *12,* 1935

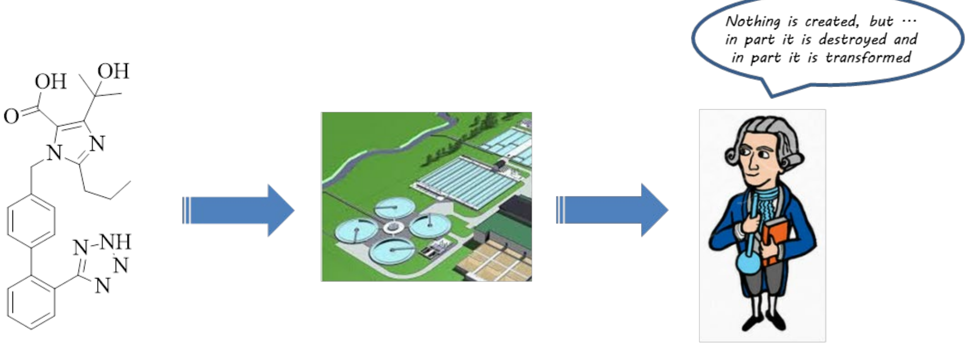
[5] F. Saliu, S. Montano, B. Leoni, M. Lasagni, P. Galli *Mar. Poll. Bull.* **2019**, *143*, 23

Characterization of degradation byproducts of Sartans: elucidation of their degradation pathway and ecotoxicity assessment[1]

Giovanni Luongo,[a] Antonietta Siciliano,[b] Giovanni Libralato,[b] Marco Guida,[b] Giovanni Di Fabio,[a] and Armando Zarrelli[a]

[a]Department of Chemical Sciences, University of Naples Federico II, 80126 Naples, Italy; [b]Department of Biology, University of Naples Federico II, 80126 Naples, Italy.

Analyses of wastewater show how the growth of the world's population goes hand in hand with an increase in the concentration of perfluoroalkyl substances, cyanobacteria, mycotoxins, hormones, pesticides, cosmetics, and industrial additives and drugs.[2] Compared to conventional organic pollutants, the concentration of these ones is much lower (ppm or ppb), and this characteristic has led to their classification as emerging contaminants (EC) and despite the low concentrations, these are persistent and potentially toxic for the environment and humans. They can be present in the water that is used to irrigate cultivation fields, and consequently in aquifers as well as in drinking water, increasing the risk of these pollutants coming into contact with the human population.[3] Most of the pharmaceutical pollutants are discharged into the environment because who takes drugs is not able to metabolize them completely. The existing treatments used for the purification of wastewater do not currently guarantee the removal of ECs, which are degraded into less harmful (but not always) compounds and only partially mineralized into inorganic substances. The use of sartans, a large and most widely used family of antihypertensive drugs, introduced in the mid-90s of the last century, has quickly spread mainly due to the alleged reduction in the incidence of certain adverse effects of varying severity (cough, angioedema,…) associated with the use of other antihypertensive agents in use until then. Their very strong commercial success together with their low metabolic degradation and high environmental persistence has consecrated them as emerging pollutants in just 20 years.



Here we present a study on different sartans, such as irbesartan,[4] Olmesartan [5] and candesartan,[6] that allowed us to draw a rather complete picture of the nature of the degradation by-products (DPs) that are obtained during the chlorination process normally used in wastewater treatment plants. Furthermore, we have been allowed to establish the sites more reactive of molecules with a basic diphenyl nucleus and a tetrazole ring as a side chain and to show the presence of common DPs, more or less recalcitrant to subsequent degradation. By 2D-NMR and MS analysis it was possible to define a possible pathway for degradation and DPs formation. Finally, we evaluated the acute and chronic toxicities of each sartan and its DPs on organisms from two levels of the aquatic food chain, *Aliivibrio fischeri* bacteria and *Raphidocelis subcapitata* algae.

[1] These studies were supported by the AIPRAS Onlus (http://www.aipras.org/).

[2] A. J. Ebele, M. A. E. Abdallah and S. Harrad, *Emerg. Contam.* **2017**, *3(1),* 1.
[3] R. Ma, B. Wang, L. Yin, Y. Zhang, S. Deng, J. Huang et al. *J. Hazard. Mater.* **2017**, *323*, 147.
[4] V. Romanucci, A. Siciliano, M. Guida et al. *Sci. Total Environ.* **2020**, *712*, 135625.
[5] G. Luongo, A. Siciliano, G. Libralato, S. Serafini et al. *Molecules* **2021**, *26(6),* 1769.
[6] G. Luongo, L. Saviano, G. Libralato, M. Guida et al. *Molecules* **2021**, 1211823.

Microalgal treatment of the liquid fraction from hydrothermal carbonization process (HTC) in a circularity perspective

M. Mantovani [1], E. Collina [1], F. Marazzi [1], M. Lasagni [1], V. Mezzanotte [1]

1 Dept. of Earth and Environmental Sciences, Università di Milano – Bicocca, P.zza della Scienza 1, 20126 Milano, Italy
** Corresponding author: m.mantovani10@campus.unimib.it*

The hydrothermal carbonization (HTC) is a low impact thermochemical process which can be used to improve the properties of different biomasses, including microalgae, providing new options for their valorization[1]. Among the by-products, the liquid fraction (HTC-LF) is the most abundant and need a proper management plan due to the potential toxicity[2, 3]. Here we propose the potential valorization of the HTC-LF obtained during the production of microalgal-based carbon-encapsulated iron nanoparticles to be used for wastewater treatment purpose. Microtox assay performed on the raw HTC-LF showed a very strong effect (EC50= 1.8% after 15 min). Given the nutrients content (Table 1), the HTC-LF was diluted with the liquid fraction of municipal digestate (Centrate) and used as growth medium to grow a mixed microalgal community in a continuous mode (HTC-LF-Centrate (20/80% v/v)). A 35-days (HRT 10 days) laboratory cultivation was performed using four columns photobioreactors (PBRs) (operative volume of 1.5 L) equipped with probes for the monitoring of temperature, pH and dissolved oxygen. CO_2 was bubbled into two reactors, under pH control (set point 7.5). Both microalgae with and without CO_2 were able to grow, having an average microalgal growth rate (rTSS) of 62 ± 5 and 43 ± 8 mg L^{-1} d^{-1}, respectively. COD removal (Figure 1) was interesting, with average percentage of 62% and 65% for the microalgae grown without and with CO_2, respectively. Finally, samples of each microalgal suspension were tested via Microtox at the end of the batch cultivation, comparing their toxicity with the one of the HTC-LF-Centrate solution used as growth medium. A substantial decrease of toxicity was observed after the microalgal cultivation. The EC50 rose from 20% in the HTC-LF-Centrate solution (IN) to 30% in the samples (CO_2 and NO CO_2). Based on the obtained result, using the HTC-LF as growth medium for microalgae seems promising allowing to decrease the overall toxicity while obtaining new biomass.

Table 1. HTC-LF characterization. All data are expressed as mean ± standard deviation (n=6)

NH_4-N (mg L^{-1})	**NO_3-N** (mg L^{-1})	**NO_2-N** (mg L^{-1})	**PO_4-P** (mg L^{-1})	**COD** (mg L^{-1})	**TSS** (mg L^{-1})	**OD680**	**pH**
490 ± 118	1.1 ± 0.8	14.4± 2.3	6.8± 0.8	2410± 184	23±20	0.1± 0.1	6.8±0.5

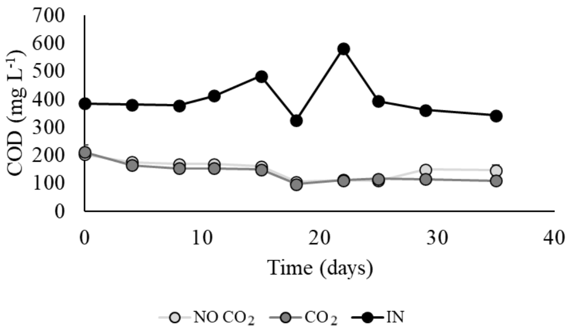


Figure 1. COD over time. Data are shown as mean ± standard error (n=2).

[1] Patel, B., Guo, M., Izadpanah, A., Shah, N., Hellgardt, K., 2016 A review on hydrothermal pre-treatment technologies and environmental profiles of algal biomass processing. Bioresour. Technol. 199, 288-299.

[2] Mihajlović, M., Petrović, J., Maletić, S., Isakovski, M.K., Stojanović, M., Lopičić, Z., Trifunović, S., 2018 Hydrothermal carbonization of Miscanthus × giganteus: Structural and fuel properties of hydrochars and organic profile with the ecotoxicological assessment of the liquid phase. Energy Convers. Manag. 159, 254-263.

[3] Usman, M., Chen, H., Chen, K., Ren, S., Clark, J.H., Fan, J., Luo, G., Zhang, S., 2019 Characterization and utilization of aqueous products from hydrothermal conversion of biomass for bio-oil and hydro-char production: A review. Green Chem. 21, 1553-1572.

Poly(diethylene 2,5-furanoate): a biobased promising candidate for compostable high-performant packaging

Giulia Guidotti[a], Silvia Quattrosoldi[a], Michelina Soccio[a], Valentina Siracusa[b], Nadia Lotti[a]

[a]*Civil, Chemical, Environmental and Materials Engineering Department, University of Bologna, Via Terracini 28, 40131 Bologna, Italy;*
[b]*Chemical Science Department, University of Catania, Viale A. Doria 6, 95125 Catania, Italy.*

The urgent issues caused by the accumulation of plastics wastes in the marine and terrestrial environment are one of the main problems of today's societies. With the goal of reducing these concerns and build a new circular economy, both the use of renewable resources for plastic production and plastic waste recycling are the most suitable solutions, according also to the European Commission directives, aiming to achieve the so called "zero-landfilling" [1]. In this framework, furan-based polyesters are particularly suitable to realize a mono-material packaging, combining bio-based origin with excellent mechanical and barrier properties, features which are particularly important in the field of packaging, the most demanding sector in terms of plastic consumption, covering alone almost the 40% of the total plastic demand [2]. In the present contribution, a fully biobased high molecular weight furan-based homopolymer, poly(diethylene 2,5-furanoate) (PDEF), was successfully synthesized by a solvent-free polycondensation process, starting from the dimethyl ester of 2,5-furandicarboxylic acid and diethylene glycol. More in details, the glycolic subunit of PDEF contains a central ether oxygen atom (Figure 1). For this reason, PDEF can be considered as derived from poly(butylene 2,5-furanoate) (PBF) (an ether oxygen atom in the middle of the glycolic subunit was added) or, alternatively, from poly(pentamethylene 2,5-furanoate) (PPeF) (an ether oxygen atom replaced the central methylene group of the glycol subunit).
After a preliminary molecular (by ^{1}H-NMR and GPC) and thermal (by DSC and TGA) characterization, mechanical (by tensile tests) and gas barrier properties (to O_2 and CO_2, measured at different temperatures and humidity conditions) of compression moulded PDEF film were also investigated. All the results obtained were compared to those previously determined for PBF and PPeF [3], in order to evaluate the effect on the final properties of the introduced chemical modification, related to the small dimensions and the high electronegativity of ether oxygen atom. After storage at room temperature for one month, both PDEF and PPeF films were completely amorphous, while PBF one developed a 3D-ordered crystalline phase. Glass transition temperature and mechanical properties of PDEF were intermediate between those of PBF and PPeF. As regards thermal stability and hydrophilicity, PDEF turned out to be the most thermally stable and hydrophilic among the polyesters under study. In addition, gas barrier performances of PDEF were very similar to those of PPeF. Lab scale composting experiments indicated PDEF as well as PPeF were compostable, the former degrading faster.

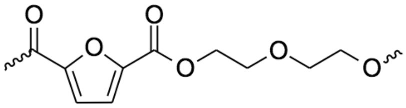


Figure 1. Chemical structure of poly(diethylene 2,5-furanoate)

[1] European Commission - A european strategy for plastics in a circular economy; 2015, https://ec.europa.eu/environment/circular-economy/pdf/plastics-strategy-brochure.pdf
[2] Plastics Europe - Plastics the Facts; 2020, https://www.plasticseurope.org
[3] G. Guidotti, M. Soccio, M.C García-Gutiérrez, T. Ezquerra, V. Siracusa, E. Gutiérrez-Fernández, A. Munari, N. Lotti, *ACS Sustain. Chem. Eng.* **2020**, *8*, 9558.

Lipids extraction from sewage sludge using green biosolvent for a sustainable production of biodiesel

Valeria D'Ambrosio, Carlo Pastore

Water Research Institute (IRSA), National Research Council (CNR), Bari, Italy

Sewage sludge is an urban waste generated in large quantities in wastewater treatments. This waste can be considered a source of lipids, which can be converted into biofuels. Recovery of lipids from sludge is the critical step in the overall process and the choice of the extracting solvent should satisfy efficiency as well as sustainability criteria.

This study reports the experimental optimisation of the extraction of lipids from wet primary sewage sludge (TS: 7.8%wt) using ethyl butyrate as extracting green solvent. Extraction conditions were optimised using the desirability function applied on the response surface methodology analysis of a Box–Behnken factorial design of experiments: extraction time (1-7 h), extraction temperature (25-70 °C), acid to alkalinity molar ratio (0-2 mol HCl/mol $CaCO_3$) and solvent to sludge weight ratio (0.25-1 g/g) were selected as factors; recoverability of trans-esterifiable lipids as the response. By carrying out the extraction at 70 °C for 7 h, using an amount of solvent equal to the wet sludge and without using any acids, almost 90% of the starting trans-esterifiable lipids were recovered (Figure 1). These extracted lipids were then efficiently converted into biodiesel through direct esterification promoted by $AlCl_3{\cdot}6H_2O$ (extract: methanol: $AlCl_3{\cdot}6H_2O$ 1:10:0.05 molar ratio), obtaining a biodiesel yield of almost 95% of the yield obtainable using HCl as a catalyst. Furthermore, the residual sludge obtained after the extraction, differently from the one obtained using hexane as extracting solvent, was found anaerobically digestible without any inhibition (Figure 2), allowing possible further exploitation of the sludge for the production of biogas. According to these results, ethyl butyrate could be considered a promising route to recover resources from sludge in a sustainable way.

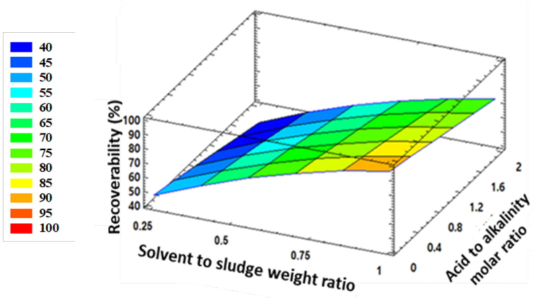


Figure 1. Response surface plot of the combined effects of solvent to sludge weight ratio and acid to alkalinity molar ratio (time = 7 h, temperature = 70 °C).

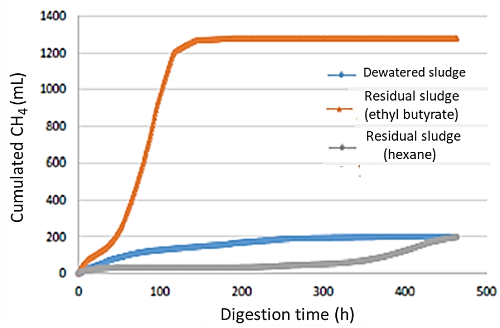


Figure 2. Cumulative methane production of dewatered sludge and residues after extraction with hexane and ethyl butyrate.

The evolving perspective on the study of ancient bronze coins

Francesco Abate[a,b]*, Giulia Franceschin*[a]*, Matteo Bettuzzi*[c]*, Fauzia Albertin*[c]*, Maria Pia Morigi*[c]*,*
Salvatore Daniele[b] *and Arianna Traviglia*[a]

[a] *Center for Cultural Heritage Technology (CCHT), Istituto Italiano di Tecnologia (IIT), Via della Libertà 12, 30175 Venezia, Italy;*
[b] *Dipartimento di Scienze Molecolari e Nanosistemi (DSMN), Università Ca' Foscari Venezia, Via Torino 155, 30172 Mestre, Venezia, Italy;*
[c] *Dipartimento di Fisica ed Astronomia "Augusto Righi", Università di Bologna, Viale Berti Pichat 6/2, 40126 Bologna, Italy;*

The present contribution aims at stimulating the community discussion, underlining the key challenges that archaeometry of ancient bronze coins presently faces. The marriage between numismatics and chemistry has been so far a long-lasting and successful relationship. The application of analytical methods to ancient coins has supplied numismatists with a plethora of data that they ably correlate and decode in historiographic, sociographic and political information on ancient civilizations [1]. This statement stands solidly when speaking of gold and silver pieces, but it falls behind for coins made out of bronze or other copper-based alloys. After centuries in a burial environment, copper alloys often show thick alteration layers. These *patina*s are much different from the original material, and can hinder the capability of common non-invasive methodologies for investigating the bulk [2]. Because of the complex stratified structure of *patina*s, similar arguments hold for the evaluation of corrosion history and conservation status, a valuable topic for conservation scientists. For these reasons, the invasive approach is still very popular for the study of archaeological metals, whereas its presence in modern archaeometric protocols is steadily decreasing. Different kinds of micro-invasive sampling – where 'micro' can variously stand from units to hundreds of microns or even above – have also been tested, with mixed results. Neutron based techniques are able to overcome these limitations [3] but they are also time consuming, and the access to neutron facilities is still limited.

The complex task of obtaining the desired information from the above unevenly stratified structures, without visibly damaging the artefact, requires smart strategies. The integration of multiscale data collected with a targeted multi-analytic approach has the potential for answering such a need. Starting from these observations, an outlook on recent methodologies will be presented. It will focus on XRF analysis, Focused Ion Beam and X-Ray Tomography as valuable tools for multiscale investigations, in the perspective of renewing and modernizing analytical protocols for the study of archaeological bronze coins. The building of modern protocols is the key enabling step for combining recent technological advances with the mining of data from our historical assets, data that can enlighten our past and help preserving our heritage for next generations.

[1] M. J. Ponting, *The Oxford Handbook of Greek and Roman Coinage* **2012**, pp. 12-30.
[2] C. Canovaro, I. Calliari, M. Asolati, F. Grazzi and A. Scherillo, *Appl. Phys. A* **2013,** *113*, 1019.
[3] G. Festa, G. Romanelli, R. Senesi, L. Arcidiacono, C. Scatigno, S. F. Parker, M. P. M. Marques and C. Andreani, *Sensors* **2020**, *20*, 502.

Investigation of the corrosive effects of ambient particulate matter on bronze through accelerated sampling and ageing

Cecilia Velino[a], *Cristina Chiavari*[b], *Carla Martini*[c], *Arianna Ercolani*[a], *Ivano Vassura*[a], *Elena Bernardi*[a]

[a]*Dept. Industrial chemistry "Toso Montanari", University of Bologna, Italy;* [b]*Dept. Cultural Heritage, University of Bologna, Italy;* [c]*Dept. Industrial Engineering, University of Bologna, Italy.*

Among the wide number of works concerning the deterioration of outdoor metallic materials, a systematic study on the effects of particulate matter (PM) is currently missing, mainly due to the complexity of the topic. In fact, PM concentration, composition and the environmental conditions vary significantly in space and time. Moreover, different parts of the same artifact could interact with different deposition fluxes depending on the geometry of exposure. Hence, the aim of this work is to investigate the effect of ambient PM on bronze corrosion in a controlled environment. For this purpose, an accelerated sampling system was set up to quickly collect significant amounts of ambient PM on metallic substrates, then the specimens with PM deposition were exposed to accelerated ageing in a climatic chamber. Two different seasonal campaigns were planned and performed, in order to collect the widest range of PM composition and concentration. For each sampling, ambient PM was collected at the same time on two sets of bronze specimens (Cu-5Sn-5Zn-5Pb, i.e. G85-5-5-5). After the sampling process, the amount of PM collected on each specimen was determined and one set was immediately extracted in ultrapure water to analyse the composition of the PM soluble fraction. The most common anions and cations (NO_3^-, NO_2^-, SO_4^{2-}, Cl^-, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, K^+) were analysed by ion chromatography (IC); total carbon was determined using a combustion analyser; the main alloying element (Cu) contained in the deposit was determined by atomic absorption spectroscopy (AAS). The second set underwent accelerated ageing in a climatic chamber programmed to expose the specimens to periodic variations of temperature, relative humidity and UVA irradiation, simulating daily cycles. During the ageing process the specimens were periodically observed by optical microscopy (OM), while at the end of the ageing the surfaces were characterized by different techniques (OM, SEM/FEG, EDS, IR, Raman spectroscopy, Vis-spectrophotometry for color analysis). Corrosion products were then removed to determine their metal content, as well as mass loss and changes in the surface profile. Qualitative and quantitative results, processed also by statistical analyses, allowed to identify the main relationships among PM features (such as composition and concentration) and bronze corrosion behavior during artificial ageing.

The leading role of diagnostics for cultural heritage in historic studies and conservation: Sarezzano reliquary busts as a case study

Maria Labate[a] *, Carmela Sirello, Fulvio Cervini* [b] *, Maurizio Aceto*[c]*, Simonetta Castronovo*[d]*,*
Lorenza Operti[a]*, Angelo Agostino*[a]

[a] *Università degli Studi di Torino, Dipartimento di Chimica;* [b] *Università degli Studi di Firenze,*
Dipartimento di Storia, Archeologia, Geografia, Arte e Spettacolo; [c] *Università del Piemonte Orientale,*
Dipartimento di Scienze e Tecnologia;[d] *Museo Civico d'Arte Antica di Torino*

Diagnostics for cultural heritage plays a crucial role in art historical research and as a fundamental phase for the restoration planning. Despite this, analysing materials is nowadays just an optional choice, closely linked to the sensitivity of professionals involved in conservation processes and to the awareness of scientific investigation to provide relevant information on artifacts' genesis, production technology and conservation history together with essential indications for conservation purpose.

The interdisciplinary study on Sarezzano(AL) reliquary-busts is a perfect example of the necessity to get the material characterization a recurring common practise in historical studies and a mandatory step in conservation assessment. The study on materials of the reliquary-busts was performed by non-invasive (X-ray fluorescence spectrometry) and micro-invasive methods (stereomicroscope, total reflection fourier transform infrared spectroscopy, powder X-ray diffraction analysis).

According to the results the busts were found to be made of tin-lead alloy, a very unusual material for medieval reliquary busts. Moreover the results suggest the busts were originally silvered, except hair and beard which are still gilded.

The outcome indicates the use of colophony as coating adhesive on the busts' alloy [1] and inside them as a consequence of the metal working process, since it is found as degraded residue [2]. Finally even the typology of alloy decay is defined [3][4].

All of this information has enabled us to define the artistic technique, the estimated value and quality of material employed.

In addition, it has led in the choice of materials and methods to adopt during the restoration, therefore more suitable solvents and tools.

[1] P. Martin-Ramos *et al.*, *BEMS. Rep.*, **2018**, *4*, 1, 03-06.
[2] V. Beltran *et al.*, *Anal. Bioanal. Chem.*, **2016**, 408, 4073-4082.
[3] H.J. Plenderleith, R.M. Organ, St. Conv., **1953**, 1, 2, 63-72.
[4] N.D. Burns, *J. Fail. Anal. and Preven.*, **2009**, *9*, 461-465.

Characterization of bacteria community on bronze and marble statues

A.Timoncini[a], E. Bernardi[b], C. Martini[c], F. Costantini[d], F. P. Mancuso[e], K. O. Matterson[d], E. Sassoni[f], C. Chiavari[a]

[a]Department of Cultural Heritage, University of Bologna, Via degli Ariani 1, 48121 Ravenna, [b]Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale del Risorgimento 4, 40136 Bologna [c]Department of Industrial Engineering, University of Bologna, [d] Department of Biological, Geological and Environmental Science, Univiersity of Bologna, Via Sant'Alberto 163, 48123, Ravenna, [e]Department of Earth and Marine Sciences, University of Palermo, Viale delle Scienze Ed. 16, 90128 Palermo, Italy, [f]Department Of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, Via Terracini 28, 40131, Bologna.

Epilithic bacteria play a fundamental role in the conservation of cultural heritage materials. Bacteria communities cause stone degradation by chemical dissolution/precipitation of substrate ions, biochemical redox reactions, organic and inorganic acid release, discoloration of the surface and physical alteration. In some cases, they also exert bioprotection actions. Bronze biocorrosion in non-burial conditions is rarely studied. The present study aims to characterize the bacteria community on bronze and stone statues via DNA analysis through 16 S RNA genes using the MinION nanopore sequencer. The samples are four swaps for the exposed and non-exposed surfaces to rainfall per statue, in three cities: Rimini, Ravenna and Bologna. Collected data will be used for generating a bacteria library. Taxonomy assignment will be performed in Mothur v. 1.39.5 using the Silva v132 as reference database. We expect different bacterial communities in each city, as well as in exposed and non-exposed conditions (sheltered/unsheltered areas on the surface of the monument).

References

[1] Dyda, M.; Decewicz, P.; Romaniuk, K.; Wojcieszak, M.; Sklodowska, A.; Dziewit, L.; Drewniak, L.; Laudy, A. Application of Metagenomic Methods for Selection of an Optimal Growth Medium for Bacterial Diversity Analysis of Microbiocenoses on Historical Stone Surfaces. *International Biodeterioration & Biodegradation* **2018**, *131*, 2–10. https://doi.org/10.1016/j.ibiod.2017.03.009.

[2] Mazzoli, R.; Giuffrida, M. G.; Pessione, E. Back to the Past: "Find the Guilty Bug—Microorganisms Involved in the Biodeterioration of Archeological and Historical Artifacts." *Appl Microbiol Biotechnol* **2018**, *102* (15), 6393–6407. https://doi.org/10.1007/s00253-018-9113-3.

Laser Ablation ICP-MS elemental imaging to investigate corroded surfaces of ancient glass

Roberta Zanini[a,b], Giulia Franceschin[a], Alessia Artesani[a] Marco Roman[c], Ligia Maria Moretto[a,b], Elti Cattaruzza[b], Arianna Traviglia[a]

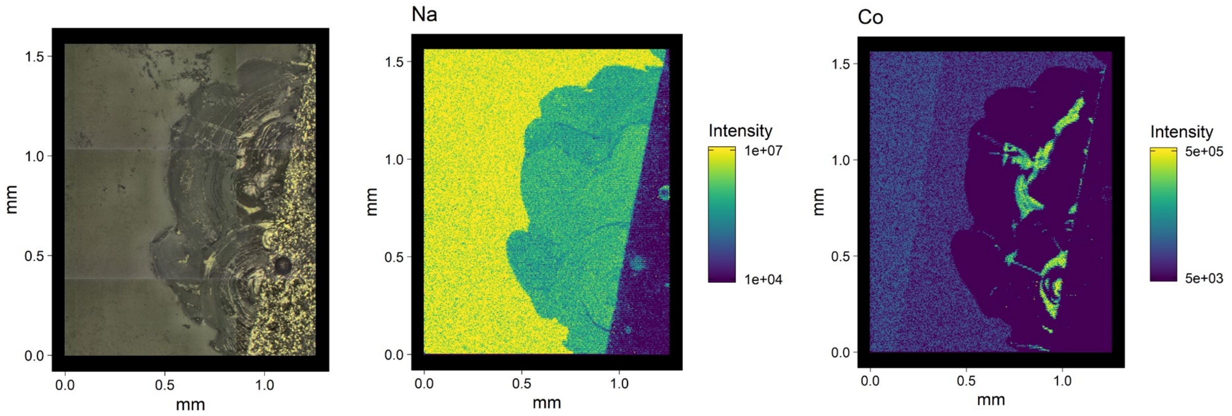
[a] *Center for Cultural Heritage Technology, Istituto Italiano di Tecnologia, Marghera (VE) Italy;*
[b] *Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari di Venezia,30170, Venezia Mestre, Italy;*
[c] *Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari di Venezia, 30170, Venezia Mestre, Italy;*

The partial or total physicochemical transformation of historical glass constituents into corroded products can induce different indicators of alteration that are detectable on its surface, such as iridescence, opalescence, pitting, and crizzling [1]. Notwithstanding the large body of research on historical objects, much remains unclear about the complex mechanism of glass degradation. In this work, we employed laser ablation-ICP-mass spectrometry as a means to obtain in-depth elemental imaging of altered layers and investigate glass weathering mechanism.

The concentration gradient of multiple elements, from the surface to the bulk pristine glass, was captured by multiple ablations on degraded regions of interest in order to highlight the dissolution of the glass network due to the hydration and leaching processes. Silica-soda-lime glass fragments, affected by several corrosion indicators, were studied using multiple raster-scanning ablation with high depth and lateral resolution. Using this procedure, we collected images of each ablated layer, and monitored the chemical distribution of elements that indicates an enrichment of silicon and a depletion of alkaline/earth alkaline ion concentration in the first few microns of depth under the surface area. The maps clearly showed the presence of sharp concentration gradients of leached-out ions between the pristine glass and the altered surface layers, and the preferential distribution of Co and Mn within certain areas (Figure 1), suggesting the possible occurrence of cyclic dissolution-reprecipitation processes [2].

Multi-elemental LA-ICP-MS imaging of altered glass turned out to be a useful method to investigate the corrosion process of ancient glass. The layer-by-layer elemental distribution shows how the composition changes from the bulk to the surface of the samples, thus providing information about the kinetic of the corrosion mechanism. The results obtained for weathered ancient glass support de-alkalinisation as the main phenomenon occurring at the glass surface in burial conditions.

[1] N.A.R. van Giffen, S.P. Koob, Encycl. Archeol, Sci (2018) 1-4. DOI: 10.1002/9781119188230.saseas0179.
[2] C. Lenting et al., Npj Mater. Degrad. 2 (2018). DOI: 10.1038/s41529-018-0048-z.



A new analytical strategy for the characterization of diagenetic pathways in ancient bones and teeth.

L. Gatti[1], F. Lugli[2], M. Zangheri[3], G. Sciutto[1], S. Prati[1], M. Mirasoli[3], S. Silvestrini[2], S. Benazzi[2], P. Iacumin[4], M. Guardigli[3], A. Roda[3,5], R. Mazzeo[3]*

[1] *Department of Chemistry "Giacomo Ciamician" Alma Mater Studiorum – University of Bologna - Ravenna Campus, Via Guaccimanni, 42 - 48121 Ravenna, Italy*
[2] *Dipartimento di Beni Culturali, University of Bologna – Ravenna Campus, Via degli Ariani, 1 – 48121 Ravenna, Italy*
[3] *Department of Chemistry "Giacomo Ciamician" Alma Mater Studiorum – University of Bologna, Via Selmi 2, Bologna, 40126, Italy*
[4] *Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parma, Italy*
[5] *Interuniversity Consortium "Istituto Nazionale Biostrutture e Biosistemi" (INBB) - Viale delle Medaglie d'Oro 305, 00136 Roma, Italy*

Bones and teeth are biological archives, and are crucial to reconstruct human past life. Unfortunately, their structure and composition are subjected to alteration overtime due to biological and chemical degradation. During the diagenesis, mineral fraction may be affected by the penetration of ground waters into the archaeological remains, which induce apatite recrystallization and changes in isotope and elemental composition. Moreover, hydrolysis may induce the breakage of the peptide bonds, leading to the decomposition of proteinaceous materials. It is known that thanks to the mutual protection between mineral and organic fractions, bones and teeth which usually show a limited diagenetic overprint, ultimately present a better conservation of the organic fraction as well [1-2]. However, the understanding of the correlation between elements variations and presence of collagen in the same specimen is still unclear.

To fill this gap, we combined the results related to elemental and collagen distribution obtained with Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) and a chemiluminescent (CL) immunochemical protocol, respectively. Immunochemical methods exploit the high specificity of the antigen–antibody recognition reaction and high sensitivity of CL detection, ensuring the direct and univocal detection of collagen. LA-ICP-MS permits the quantitative investigation of trace elements and rare earth elements exploring sample surfaces [3].

To evaluate the integration between the two techniques, teeth and bones from various archaeological contexts, chronological period, and characterized by different collagen content were analyzed. Immunochemical results revealed a heterogeneous distribution of collagen, especially in highly degraded samples. Subsequently, LA-ICP-MS was performed to evaluate the distribution of elements and isotopes, showing a correlation between the presence of U and rare earth element and areas with low amount of collagen. The innovative integration between immunochemical CL method and LA-ICP-MS analysis permitted to clarify the mutual relation between elements variation and collagen preservation overtime, with consequent useful information to unravel the effects of diagenetic alteration in bones and teeth.

[1] C. Kendall, A.M. H.Eriksen, I. Kontopoulos, M.J. Collins, G. Turner-Walker, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2018**, *491*, 21-37.

[2] P.V. Ulmann, K.K. Voegele, D.E. Grandstaff, R.D. Ash, W. Zheng, E.R. Schroeter, M.H. Schweitzer, K.J. Lacovara, *Sci. Rep.* **2020**, *10 (1)*, 15566.

[3] M.C. Sforna, F. Lugli, *J. Anal. At. Spectrom.* **2017**, *32*, 1035.

Archaeometric investigation on Roman frescoes from the archaeological site of Aquileia

Raffaella Lamuraglia [a,b]*, Alessia Artesani* [a]*, Chiara Coletti*[c]*, Claudi Mazzoli*[c]*, Federica Menegazzo*[b]*, Arianna Traviglia* [a]

[a] *Center for Cultural Heritage Technology, Istituto Italiano di Tecnologia, 30175 - Marghera (VE) Italy;*
[b] *Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, 30170, Venezia Mestre, Italy;*
[c] *Dipartimento di Geoscienze, Università degli Studi di Padova, 35131, Padova, Italy.*

This work reports the results of a multi-analytical study of 21 fragments of Roman mural frescoes found during an archaeological prospection on agricultural fields in the outskirts of a major ancient Roman city, Aquileia (Italy). The research aimed at characterising the entire stratigraphy (mortars and pictorial layers) of the archaeological samples, in order to increase our knowledge of the production technologies, working techniques and provenance of raw materials in Roman age [1].
The petrographic and textural characterization of the thin section mortars were performed analysing the distribution and morphology of the mineral grains and pores, the presence of lumps, as well as the binder/aggregate ratio, with the aid of a Polarised Optical Microscopy (POM) and Scanning Electron Microscopy equipped with an Energy Dispersive X-ray detector (SEM-EDX). The results highlight a fine carbonate matrix containing spatic calcite grains in the *intonaco* mortar, where the aggregate tends to be more angular shaped than in the preparatory layers. Secondary calcite crystals within pores (mainly *vughs*) were observed, derived by dissolution and recrystallization processes. The presence of lumps reveals also that the lime was produced using the *fusion* method, the traditional technology for preparing the mortar binder that employs the slaking of the quick lime clods [2].
The fresco painted layers were clearly distinguishable when observed under optical microscope, showing a preponderance of red and yellow pigments, identified as hematite and yellow ochres by μ-Raman and SEM EDX. The common use of these pigments, the composition and morphology of the mortar layers led to hypothesise that the archaeological fragments did not belong to a prestigious building, but rather to common houses [3]. The results of the characterisation of these fragments, while contributing to define some aspects of the house estates in the territory of Aquileia, will serve for the development of mock-ups on which to test protective layers aimed at preserving fresco surfaces.

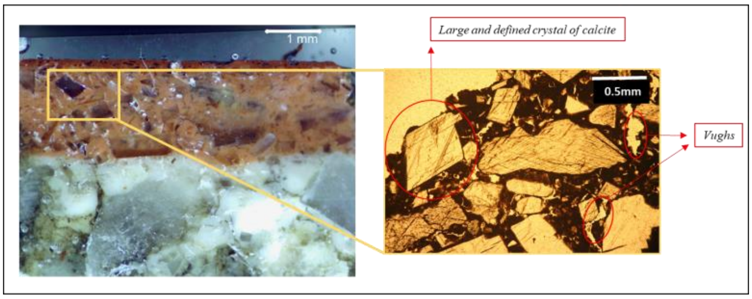


Figure – (left) Image (magnification 2x) acquired at NIKON stereoscope SMZ745T of cross section of an archaeological mural frescoes found in the outskirt area of Aquileia (NE, Italy). (right) Photomicrograph in transmitted plane-polarized light using a Nikon Eclipse ME600 instrument.

References

[1] Fabio, S., et al. (2020). Archaeological and Anthropological Sciences, 12(7), 1-23.
[2] Pecchioni, E., et al. (2014). Nardini Editore, Firenze, 78.
[3] Ling, R. (1991). Roman painting. Cambridge University Press.

Diammonium hydrogen phosphate and Ca (OH)$_2$ nanoparticles for consolidation of ancient bones: evaluation of performances

Francesca Porpora[1], Valentina Zaro[2], Giulia Marradi[1], Arianna Meoli[1], Luigi Dei[1], David Caramelli[2], Martina Lari[2], Emiliano Carretti[1]

[1]Department of Chemistry "Ugo Schiff" and CSGI, University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino, FI, Italy; [2]University of Florence, Department of Biology, via del Proconsolo 12, 50122 Firenze, Italy

Archaeological and paleontological bones are peculiar and precious finds. Due to the improvement in the last few decades of many new technologies, such as ancient DNA sequencing, skeletal remains can be considered as a true "Biological Archive" that should be accessible for long-term studies: in addition to historical and archaeological information, biological data offer a fundamental resource to reconstruct the history and the uses of past human populations [1, 2].

Archaeological bones are typically discovered in critical storage conditions and, since the twentieth century, the products typically used for consolidation treatments are natural and synthetic organic polymers [3]. Unfortunately, their scarce physico-chemical compatibility with the substrate and their low chemical stability, which results in depolymerization and cross-linking reactions, can lead to a rapid decrease of their performance and dangerous alterations for the bone matrix (such as yellowing and mechanical stresses). In addition, their degradation seriously limits their removal and the re-treatability of the object. Moreover, the application of organic polymers may compromise future molecular analysis such as radiocarbon dating, isotope analysis and paleogenetic analysis [3, 4].

On these bases, the main aim of this study [5] is to develop an effective consolidation treatment that at the same time preserves the integrity of these relics and ensures their fruition without compromise the following molecular analysis. The approach purposed is based on the application of inorganic materials with high physical-chemical compatibility with the substrate. In particular, an aqueous solution of diammonium hydrogen phosphate (DAP) has been used as a precursor agent for the growth of a 3D crystalline network of hydroxyapatite (HAP) in degraded ancient bones. The consolidation performance of the HAP has been evaluated also after a pre-treatment with Ca(OH)$_2$ nanoparticles (NPs), successfully used in the last years for the consolidation of both carbonatic matrixes of artistic interest and bone relics [6, 7]. The *in-situ* precipitation of HAP with or without pre-treatment with Ca(OH)$_2$ NPs influences the overall porosity as we can see from the adsorption-desorption isotherms obtained through the Brunauer Emmet and Teller (BET) theory that indicate a decrease of surface area and pore volume of 45% and 64% respectively. Furthermore, the formation of a homogeneous dense phase after the treatment was showed in X-ray microtomography images and was confirmed by the increase of the Vickers microhardness (more than 40%). It was also showed that the color change induced on the surface of treated samples is not perceivable by the human eye ($\Delta E<2$). Finally, through paleogenetic analysis, we observed that authentic genetic data could be obtained from degraded bones even after the consolidating treatments.

[1] L. Weyrich, S. Duchene et al., *Nature*, **2017**, *544*, 357.
[2] F. Tassi, S. Vai et al., *Proc. R. Soc. B: Biological Sciences*, **2017**, *284,* 20171540.
[3] J. Johnson, *Journal of Field Archaeology*, **1994**, *21*, 221.
[4] I. Natali, P. Tempesti et al., *Languir*, **2014**, *30*, 660.
[5] A. Salvatore, S. Vai et al., *Journal of Cultural Heritage*, **2019**, *41*, 1.
[6] D. Chelazzi, G. Poggi et al., *Journal of Colloid and Interface Science*, **2013**, *392*, 42.
[7] I. Natali, P. Tempesti et al., *Langumuir*, **2014**, *30*, 660.

Discovering the Maya ritual practices through the study of pigmented human bones remains by Archaeometry investigation

Rigon Carolina[a], *Vázquez De Ágredos Pascual Maria Luisa*[b], *Izzo Francesca Caterina*[a]

[a]*Sciences and Technologies for the Conservation of Cultural Heritage, Department of Environmental Sciences, Informatic and Statistics, Ca' Foscari University of Venice, Via Torino 155/b, Venice, Italy*
[b] *Departamento de Historia del Arte, Universitat de València, Av. Blasco Ibañez 28, Valencia, Spain*

As several archaeological finds witnessed, treating dead bodies with ointments during funeral rituals was a common practise among ancient Mayans. These substances assumed a deep symbolic connotation and probably their application had also a preservative purpose. Bodies needed to be prepared to face their entry to the *Underworld*, the place where dead persons went after death according to Maya beliefs. In fact, Mayans used to cover the corpses, totally or partially, with red pigments presumably by: a) dusting them directly on the bodies; b) applying them in the form of ointments – sometimes scented too (pigments were mixed with organic binders); c) impregnating textiles with natural resins to wrap the corpses (similar to shrouds) and then covered them with pigments [1] [2] [3]. Research on pigments used by Mayans have been increasing during the last years but there is still so much to discover especially regarding the organic binders used in these ointments formulation and used to prepare textiles as well.

The aim of this study has been the archaeometry investigation of the pigments and the organic binders used in some partly pigmented human bones remains coming from the archaeological sites of Calakmul and XCambó situated in Mexico. Bones fragments exhibited well-preserved red and red-brownish areas. UV-VIS spectroscopy and EDX analysis provided significant information that allowed to recognize two main categories of pigments: Red Earth (Fe_xO_x) or more probably Ochre ($Al_2O_3SiO_2 * H_2O$) and Cinnabar (HgS).

Thanks to GC/MS and THM-Py-GC/MS analysis, the organic fraction has been identified as animal fat (especially in the samples of Calakmul site) because of the presence of linear saturated fatty acids. The detection of the isoprene structure suggested the presence of a natural gum probably extracted from *Hevea Brasiliensis* tree since some of its amyrin typical compounds were detected. This is a common specie in Central America area and it was easily available to ancient Mayans. In some samples a series of dicarboxylic acids (specifically suberic and azelaic acids) suggested the presence of a vegetable drying oil, presumably Chia Oil. The pyrogram of one sample coming from XCambó site showed the presence of some alkanes and alkenes and an aromatic fraction that can be related to a bituminous material.

The physicochemical investigation of the organic fraction can be considered the real innovation of this research because of the lack of information available on this topic. This lack is partially due to the difficulties of identifying and detecting organic compounds in samples significantly affected by diagenesis phenomena related to inhumation condition in which archaeological samples are generally remained for centuries.

[1] Batta et al., *On yellow and red pigmented bones found in Maya burials of Jaina*, Journal of Archaeological Science **2012**, pp. 1-11

[2] Vázquez de Ágredos Pascual M.L., *Body Colors and Aromatics in Maya Funerary Rites*, **2018**, in Painting the Skin. Pigments on Bodies and Codices in Pre-Columbian Mesoamerica (Élodie Dupey & María Luisa Vázquez de Ágredos, Eds.), pp. 11-23, The University of Arizona Press-Universidad Nacional Autónoma de México.

[3] Rigon C., Izzo F.C., Vázquez de Ágredos Pascual M.L., Campíns-Falcó P., Van Keulen H., *New results in ancient Maya rituals researches: the study of human painted bones fragments from Calakmul archaeological site (Mexico)*, **2020**, Journal of Archaeological Science: Reports

The assessment of the organic composition of historical remedies and drugs through a multidisciplinary approach

Giulia C. Lodi [a,*], *Giuseppe Borsato* [b], *Ma. Luisa Vázquez de Ágredos Pascual* [c], *and*

Francesca C. Izzo [a]

[a] *Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Via Torino 155/b, 30174 Mestre, Venezia, Italy.*
[b] *Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Via Torino 155/b, 30174 Mestre, Venezia, Italy.*
[c] *Department of Art History, Faculty of History and Geography, University of Valencia, Av. Blasco Ibañez 28, 46010 Valencia, Spain.*
[*] *Presenting author*

This contribution is part of an interdisciplinary project focused on the study, valorization, conservation and musealisation of the historical remedies and drugs conserved in the *Spezieria di Santa Maria della Scala*, located in Rome, and founded in 1700 by the order of the Discalced Carmelite friars. The entire *Spezieria,* considered both for its content and its architectonic value, is an outstanding case of Cultural Heritage that deserves to be investigated and preserved.

Historical research testifies that the friars were famous for controlling trade with the East and West Indies and for importing spices and other "exotic" ingredients, which they used and mixed for their formulations. Previous studies confirmed the presence of materials traditionally used as ingredients of products for medical, cosmetic and artistic use, inside the Spezieria [1] [2].

The complex organic composition of the ancient remedies stored inside the *Spezieria* was disclosed through a multidisciplinary approach: the results obtained by FT-IR spectroscopy, gas chromatography associated with mass spectrometry (GC-MS) and nuclear magnetic resonance (NMR) were combined with botanical and historical research [3] [4].

It was possible to formulate some compositional hypothesis to elucidate the use of the studied drugs formulations. Moreover, data related to the genus of plants from which these natural compounds derive and to their geographical origin were acquired.

This synergy can provide exceptional information on cosmetic, pharmaceutical and technological knowledge, usage practices and daily life in the historical context studied. The study of historical remedies is also significant as a starting point to re-propose ancient formulations that can be used as a basis for the current production of phytotherapeutic and cosmetic remedies.

Acknowledgments: M.L.V.dA.P. was sponsored by Aboca Cooperativa Agricola (Sansepolcro, Italy).

[1] M.L. Vázquez de Ágredos Pascual, G. Cavallo, R. Pagiotti, L. Rojo Iranzo, M. Souto Martín, P. Walter, E. Van-Elslande, F.C. Izzo, *Eur. J. Sci. Theol*. **2018**, *14*, 3–12.
[2] G. Cavallo, M.L. Vázquez De Ágredos Pascual, *Powder Diffr*. **2018,** *33*, 270–278. doi:10.1017/S0885715618000738.
[3] G.C. Lodi, G. Borsato, M.L. Vázquez de Ágredos Pascual, F.C. Izzo, *Anal. Bioanal. Chem*. **2020**, *412*, 7581–7593. doi:10.1007/s00216-020-02893-1.
[4] F.C. Izzo, G.C. Lodi, M.L. Vázquez de Ágredos Pascual, *Archaeol. Anthropol. Sci*. **2021**, *13*, 2 doi:10.1007/s12520-020-01236-6.

New photo-Fenton like process for roof harvested rainwater disinfection

Fiorentino[1] A., Lofrano[2] G., Cucciniello[1] R., Carotenuto[1] M., Motta[3] O., Proto[1] A., Rizzo[4] L.

[1]Department of Chemistry and Biology "A. Zambelli", University of Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy;
[2]Centro Servizi Metereologici e Tecnologici Avanzati (CeSMA), University of Naples Federico II, Via Cinthia 21, 80126, Naples, Italy;
[3]Department of Medicine Surgery and Dentistry, University of Salerno, via S. Allende, 84081, Baronissi, SA;
[4]Department of Civil Engineering, University of Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy;

To date more than 1billion people lives in area with water scarcity, and it is expected that this number will increase in 2025 up to 1.8 billion persons [1]. In the past years the water use has increased six fold over rising by about 1% per year. Roof-harvested rainwater (RW) has attracted increasing attention as valid alternatives to lessen the impacts associated with the uncontrolled use of potable water in several countries [2]. The replacement of drinking water with RWs for several non-potable uses such as toilet flushing, cars cleaning and garden watering which do not need to get drinking water standard, represent a great challenge. RWs generally have a good quality, with a low organic content, and low nutrient concentration. However, several pathogens such as Pseudomonas aeruginosa, and Acanthamoeba spp, [3], Escherichia coli (E. coli) and Enterococcus sp. (Entero) have been detected in RW [4]. The RWs are mainly treated with filtration treatments, which do not allow to remove completely pathogenic microorganisms [5] and a disinfection process is necessary for a safe reuse [6]. One of the main RWs disinfection systems is solar disinfection (SODIS) that strongly depends on UV-A radiation and therefore is not always effective [7]. On the other hand, conventional systems such as chlorination, present the disadvantage of formation of hazardous chlorination by-products (DBPs), and this pushes towards the search for alternative and potentially safer treatments such as advanced oxidation processes (AOPs) which have great potential in pathogens removal [8]. Among the AOPs, Fenton and conventional photo-Fenton have been shown to be highly effective in bacterial removal. Main constraints to their application are related to the acidification of the water, with high costs and operational problems and to energy costs [9]. In this work, chlorine and UV-C radiation, two of the most widely used conventional disinfection processes, have been compared with solar-driven AOPs for disinfection of RWs. Solar driven AOPs included a new solar photo Fenton like process with an innovative catalyst that allowed to work at neutral pH, and thus to obtain an economical treatment process. Processes behavior's were evaluated on different family bacteria strains, selected from real RW, in terms of bacterial inactivation and regrowth. According to our results, solar driven AOPs are promising options for RWs disinfection and reuse.

[1] United Nations, Water for life, 2005–2015. Water Scarcity, 2014.
[2] Ahmed, W., Gyawali, P., Toze, S., 2015Environ. Sci. Technol. 49, 3084–3090.
[3] Albrechtsen, H.-J., 2002. Water Science and Technology 46, 311–316.
[4] Hamilton, K.A., Ahmed, W., Palmer, A., Sidhu, J.P.S., Hodgers, L., Toze, S., Haas, C.N., 2016. Environmental Research 150, 320–327.
[5] Gikas, G.D., Tsihrintzis, V.A., 2012. 466–467, 115–126.
[6] Rizzo, L., Gernjak, W., Krzeminski, P., Malato, S., McArdell, C.S., Perez, J.A.S., Schaar, H., Fatta-Kassinos, D., 2020. Science of The Total Environment 710, 136312.
[7] Dawney, B., Pearce, J.M., 2012. Journal of Water, Sanitation and Hygiene for Development 2, 87–94.

[8] Fiorentino, A., Cucciniello, R., Di Cesare, A., Fontaneto, D., Prete, P., Rizzo, L., Corno, G., Proto, A., 2018. Water Research 146, 206–215.
[9] Wang, X., Hu, X., Wang, H., Hu, C., 2012. Water Res 46, 1225–1232.

Removal of contaminants of emerging concern by enzymatic treatment with fungal laccases

E. Gaggero [a], *P. Calza* [a], *G.C. Varese* [b], *F. Spina* [b], *M. Rigoletto* [a], *E. Laurenti* [a]

[a] *Department of Chemistry, University of Torino, Via Pietro Giuria 5, 10125 Torino, Italy*
[b] *Department of Life Sciences and Systems Biology, University of Torino, Viale P. Mattioli 25, 10125 Torino, Italy*

Continuous discharge of untreated domestic wastewater can cause significant environmental impacts on surface and groundwater. More than 2 million people die every year from waterborne diseases, unsafe water and lack of basic sanitation. In the last decades, concern arose for the presence in wastewater, surface water and groundwater of the so called "Contaminants of Emerging Concern" (CECs). CECs include pharmaceuticals and personal care products (PPCPs), endocrine-disrupting compounds (EDCs), flame retardants (FRs), pesticides, and artificial sweeteners (ASWs), all sharing a poor removal during the conventional wastewater treatment plants, which results in their introduction in the environment [1]. Therefore, these partially polluted waters could indirectly re-enter the food chain and pose hazard for human health and aqueous ecosystems. In light of the above, the strengthening of existing water treatment methods and the development of new sustainable and efficient technologies for the decontamination of wastewater are needed.

The catalytic properties of oxyenzymes can be exploited for the abatement of pollutants; they can activate radical processes capable of degrading toxic molecules present in water bodies. Laccases are a type of lignin-modifying enzyme (LME) and comprise monomeric, dimeric or tetrameric glycoproteins with four copper atoms per monomer located at the catalytic site. Laccases have a wide substrate range, which can serve industrial purposes and/or bioremediation processes. The simple requirements of laccase catalysis (presence of substrate and O_2), as well as its apparent stability and lack of inhibition, make this enzyme both suitable and attractive for biotechnological applications [2].

In the present study we used fungal laccases produced by *Trametes pubescens* (Tp) and C*oriolopsis gallica* (Cg), which belong to the White Rot fungi ecophyfiological group. Their choice was due to their capability of producing oxidative enzymes with a remarkably high value in terms of biotechnological potential thanks to their high redox potential, low substrate specificity and high stability, that makes them able to degrade different classes of pollutants even in complex mixtures.

Initially, we tested and optimized the use of the two laccases with the aim of defining the best conditions for their use in aqueous solution. Preliminary tests were performed using 2,4,6-trichlorophenol (2,4,6-TCP) as target molecule. After these screening tests, the efficiency of the enzymatic treatment was ascertained toward other pollutants, as 2,4-dichlorophenol, atrazine, hydroxyatrazine, carbamazepine, diclofenac, bisphenol A, geosmin and 2-methylisoborneol.

Furthermore, it is important to immobilize enzymes in order to obtain stable and long-lasting systems even in the presence of complex matrices and often not optimal environmental conditions. This procedure allows to obtain an increase in the laccase stability and resistance to alkaline pH, high temperatures and inhibitors and permits the recovery and recycling of enzymes, so leading to a reduction in the cost of the treatment. Therefore, laccases were tested both in solution and immobilized on silica monoliths previously functionalized with 3-aminopropyltriethoxysilane (APTES), and the results obtained in the two conditions were compared.

[1] M. Jiménez-Tototzintle, I. Jales Ferreira, S. de Silva Dunque, P. R. Guimaraes Barrocas, E. Mendes Saggioro, *Chemosphere,* **2018**, 210, 449-457.
[2] J-A. Majeau, S. K. Brar, R. Dayal Tyagi, *Bioresour. Technol,* **2010,** 101, 2331-2350.

Zinc and Iron Based Metal-Organic Frameworks as Ofloxacin Adsorbents in Polluted Waters

Doretta Capsoni [a], *Giulia Guerra* [b], *Constantin Puscalau* [a,c], *Federica Maraschi* [b], *Giovanna Bruni* [a], *Francesco Monteforte* [a], *Antonella Profumo* [b] *and Michela Sturini* [b]

[a] *C.S.G.I. (Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase) & Department of Chemistry, Physical Chemistry Section, University of Pavia, 27100 Pavia, Italy;* [b] *Department of Chemistry, University of Pavia, 27100 Pavia, Italy;* [c] *The GlaxoSmithKline Neutral Laboratories for Sustainable Chemistry, University of Nottingham, Jubilee Campus, Nottingham, NG7 2TU, UK*

Emerging contaminants (ECs) are natural or synthetic substances that enter the environment through many pathways. Despite their low concentrations, from ng to a few µg L^{-1}, ECs are found ubiquitously in environmental waters due to the anthropic impact. Antibiotics are among the most widespread ECs, their presence causes the spread of antibiotics resistance, so it is mandatory to find new ways to remove them [1]. The project aims to study pollutants removal from contaminated waters through adsorption, a method often used for water remediation; it offers many advantages such as stability, ease of use, low costs, and excellent performance. In this work, four metal-organic frameworks have been studied, using ofloxacin (OFL) antibiotic as a model molecule.

Zeolitic Imidazolate Framework-8 (ZIF-8), the Zn(II) and benzene-1,3,5-tricarboxylate ($Zn_3(BTC)_2$), the Fe(III) and benzene-1,3,5-tricarboxylate MIL-100(Fe) (Materials of Institut Lavoisier) and Fe_3O_4@MIL-100(Fe) have good prospects as adsorbents for remediation of contaminated water thanks to an environment compatible metal ion, high surface area, and adequate adsorption capacity [2].

MOFs, prepared through facile syntheses from the literature [3-6] or appropriately designed in the case of the Fe_3O_4@MIL-100(Fe), were characterized using Fourier-transform infrared spectroscopy, X-Ray powder diffraction, thermal analysis and scanning electron microscopy analyses. Adsorption experiments were performed in tap water due to its invariant composition and a more remarkable similarity to environmental waters. Adsorption isotherms were investigated to calculate the adsorption capacity of each material, and kinetic experiments were carried out to describe the antibiotic uptake on the solid sorbents.

Results showed that OFL was adsorbed in the range 25.3 ± 0.8 - 158 ± 5 mg g^{-1} on the considered composites, following different mechanisms. According to R^2, Langmuir is the best model for ZIF-8, MIL-100(Fe), and Fe_3O_4@MIL-100(Fe) while the sigmoidal model best fits $Zn_3(BTC)_2$ experimental data. Also the kinetic results were quite different, pseudo-second-order and sigmoidal. The suitability of ZIF-8, $Zn_3(BTC)_2$, MIL-100(Fe), and Fe_3O_4@MIL-100(Fe) as adsorbent phases for water depollution was tested on tap water and river samples spiked with OFL 10 µg L^{-1}. The obtained removal efficiencies (72-90 %), indicate that these materials are promising candidates for removing fluoroquinolone antibiotics from polluted waters.

[1] S. Castiglioni, E. Davoli, F. Riva, M. Palmiotto, P. Camporini, A. Manenti, E. Zuccato, *Water Research*, **2018**, *131*, 287-298.

[2] N. Li, L. Zhou, X. Jin, G. Owens, Z. Chen, *J. Hazard. Mater.* **2019**, *366*, 563-572.

[3] Y. Pan, Y. Liu, G. Zeng, L. Zhao, Z. Lai, *Chem. Commun.* **2011**, *47,* 2071

[4] W.W. Lestari, M.Arvinawati, R. Martien, T Kusumaningsih, *Mater. Chem. Phys*. **2018**, *204*, 141–146

[5] F. Zhang, J. Shi, Y. Jin, Y. Fu, Y. Zhong, W. Zhu, *Chem. Engin. Journal* **2015**, 259, 183-190.

[6] S. Yu, J. Wan, K. Chen, *Journal of Colloid and Interface Science* **2016,** 461, 173–178.

Biodegradability enhancement of non-ionic surfactants in industrial wastewater by UV/H_2O_2 pre-treatment

S. Murgolo, C. De Ceglie, G. Bagnuolo, R. Ciannarella, G. Mascolo

CNR, Istituto di Ricerca Sulle Acque, Via F. De Blasio, 5 – 70132 Bari

Industrial wastewaters often contain non-ionic surfactants arising from several industrial productions and this has detrimental effects on their biodegradability. Specifically, the lack of surfactants biodegradation causes the effluents not to be compliant to the law limits for COD (chemical oxygen demand) and total surfactants. It follows that a tertiary step is necessary to remove residual surfactants. This can be accomplished by adsorption methods or by advanced oxidation methods, the former being not environmentally friendly and the latter being not able to easily mineralize the COD. In the present investigation the treatment of a real industrial wastewater, from a house lighting company, was carried out using UV/H_2O_2 pre-treatment in order to enhance the biodegradability of the non-ionic surfactant wastewater. The final goal of the investigation was to tailor the UV/H_2O_2 step to transform the non-ionic surfactants into biodegradable by-products and then allow a conventional biological treatment to perform the degradation of the whole COD in order to get the final effluent compliant to the law limits. This treatment set-up allows the UV/H_2O_2 and biological steps to work in a synergic way in order to keep the UV dose as low as possible in order to only transform the non-ionic surfactants without mineralizing them.

The UV/H_2O_2 treatment was carried out, in the semi-batch mode, using a 10 L UV reactor equipped with a 280 W low pressure Hg lamp. The industrial wastewater (15 L) was placed into a vessel and recirculated through the UV reactor by a centrifugal pump. H_2O_2 was added in the vessel at the proper concentration at the beginning of the reaction. Biodegradability of the effluents was monitored by measuring the COD and BOD_5.

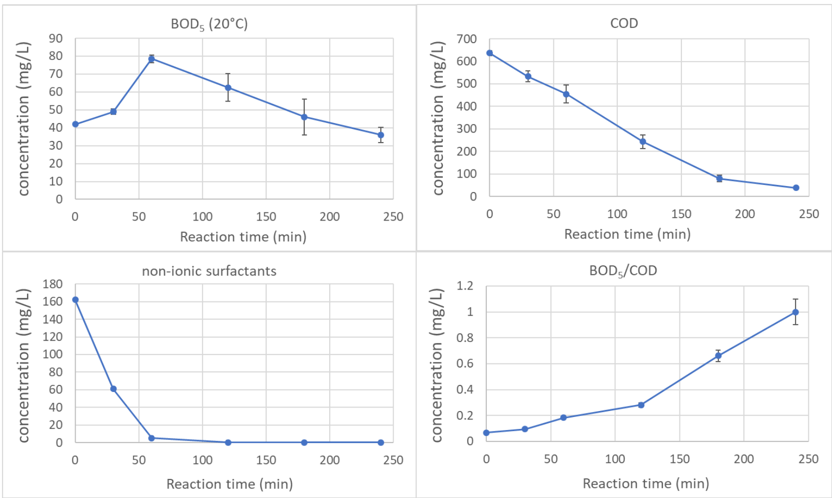


Figure 1. Results obtained from the UV/H_2O_2 treatment of the real industrial wastewater.

Results depicted in figure 1 show that the UV/H_2O_2 treatment is very effective for increasing the biodegradability of the industrial wastewater. Specifically, the BOD_5/COD ratio constantly increases with the reaction time reaching a value of 1 after 240 min. It is worth noting that a ratio of just 0.5 suggests that the resulting effluent is already biodegradable.

Acknowledgment

This work was partially supported by the Apulia Region funding the FontanApulia (WOBV6K5) project within the InnoNetwork programme.

Remediation of groundwater contaminated with PCBs and PAHs by photocatalysis employing nano-sized TiO_2 supported onto steel mesh

S. Murgolo[a]*, C. De Ceglie*[a]*, G. Bagnuolo*[a]*, R. Ciannarella*[a]*, M. Dell'Edera, A. Truppi,*[d] *R. Comparelli*[b]*, M.L. Curri*[c]*, G. Mascolo*[a]

[a]*CNR, Istituto di Ricerca Sulle Acque, Via F. De Blasio, 5 – 70132 Bari*
[b]*CNR, Istituto sui Processi Chimico Fisici, Via F. De Blasio, 5 – 70132 Bari*
[c]*Università degli Studi di Bari, Dip. Chimica, Via Orabona 4, 70126, Bari, Italy*
[d] ***TCT Nanotech** - divisione di TCT s.r.l., Strada per Pandi n. 3, 72100 Brindisi, Italy…*

Granular activated carbon (GAC) is often used to remediate polluted groundwater. However, the use of GAC is known to be a rather expensive treatment option when organics concentration is high. In addition, adsorption-based processes do not represent an environmentally sustainable solution because they merely transfer pollutants from one phase to another.

Valuable processes for the degradation of organic pollutants in contaminated groundwater are the advanced oxidation processes (AOPs). Among them photocatalysis is considered to be attractive due to the absence of chemicals to be employed. However, problems still exist due to the catalysts to be employed that are normally dispersed in the water solution and need to be removed at the end of the process. In the present work a new synthesized TiO_2-based nanosized catalyst [1], supported on a stainless steel mesh, has been used in a pilot-scale process for the remediation of a real polluted groundwater with PAHs and PCBs. The performance of the new supported catalysts was also compared with UV/H_2O_2 and photocatalysis with Degussa TiO_2 catalyst supported of the same stainless steel mesh.

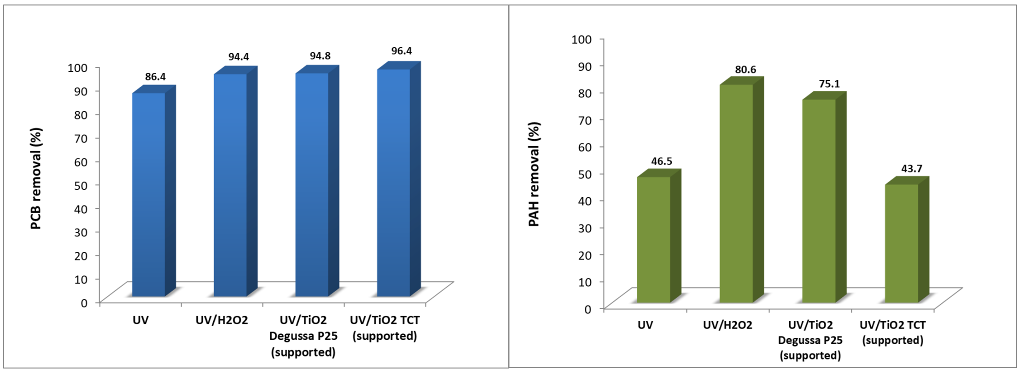


Figure 1. Results obtained at pilot scale for the degradation of main PCB congeners (18, 28, 31, 52, 44) present in the water(left pane) and PAHs (right pane) in the real contaminated groundwater.

The treatments were carried out, in semi-batch mode, using a 30 L UV reactor equipped with four 330 W low pressure Hg lamps. The contaminate groundwater (150 L) was placed into a vessel and recirculated through the UV reactor by a centrifugal pump. H_2O_2 was added in the vessel at the proper concentration at the beginning of the reaction.

The results depicted in Figure 1 show that the two supported catalysts are as effective as UV/H_2O_2 for the degradation of PCBs while, for the degradation of PAHs, UV/H_2O_2 is still the most efficient process.

Acknowledgment

This work was partially supported by the Apulia Region funding the FontanApulia (WOBV6K5) project within the InnoNetwork programme and by the Italian PON MIUR "Energy for TARANTO" (Proposal Code ARS01_00637) projects

[1] Dell'Edera et al. *Catalysts* **2020**, *10*, 89

Biogas to Syngas through the Combined Steam/Dry Reforming Process: An Environmental Impact Assessment

Nicola Schiaroli[a], Mirco Volanti[a], Antonio Crimaldi[a], Fabrizio Passarini[a], Angelo Vaccari[a], Giuseppe Fornasari[a], Sabrina Copelli[b], Federico Florit[c], and Carlo Lucarelli[b]

[a] Dipartimento di Chimica Industriale "Toso Montanari", viale del Risorgimento 4, 40136 Bologna, Italy; [b] Dipartimento di Scienza e Alta Tecnologia, via Valleggio 9, 22100 Como, Italy; [c] Dipartimento di Scienza e Alta Tecnologia, via Valleggio 9, 22100 Como, Italy

Reinventing the energy and chemical market to overcome the intensive use of fossil fuels through the efficient exploitation of renewable sources is an essential step to reduce the anthropogenic impact on the environment. In this context, a better exploitation of biogas can deal with the increasing amount of organic wastes generated by modern societies and the reduction of greenhouse gas emissions, providing a way to overtake two of the main modern life challenges. Delocalized small plants can in fact produce biogas by the anaerobic fermentation of biomasses and/or wastes through technologies such as biodigesters, landfill gas recovery systems, and wastewater treatment plants.[1,2] The composition of biogas depends on the type of feedstock processed and on the production pathway but, after its purification, it is composed of only CH_4 (45 up to 75%) and CO_2.[3] An appealing application of clean biogas lies in its valorization through gas-to-liquid systems. Through the production of synthesis gas (syngas, a mixture of H_2 and CO) as an intermediate step, it is indeed possible to produce valuable products such as methanol and/or liquid fuels via Fischer−Tropsch synthesis.

In the present work, the use of a sustainable combined steam/dry reforming (S/DR) technology to obtain syngas from clean biogas is proposed. Starting from the laboratory data obtained in the industrial conditions, mass and energy balances for the overall process were obtained from Aspen HYSYS simulations. In order to evaluate its environmental qualities, it has been compared with the current syngas production technology (ATR, Autothermal Reforming) using different solutions with both biogas and natural gas. Fig. 1 shows the created scenarios and the system boundaries of the study. The environmental evaluation was performed by applying the Life Cycle Assessment (LCA) methodology and the analysis showed that clean biogas-to-syngas technology using reforming processes has the potential to reduce the anthropogenic impact on the environment. The ReCiPe method showed that when the combined S/DR process is conducted using clean biogas also as a heat source, the CO_2 balance turns negative, ensuring that the whole process has excellent potential as Carbon Capture and Utilization (CCU) technology providing the lowest damage in all categories. Its improvement would make it possible to further reduce the environmental burden of the overall process, which is essential for achieving sustainable development.

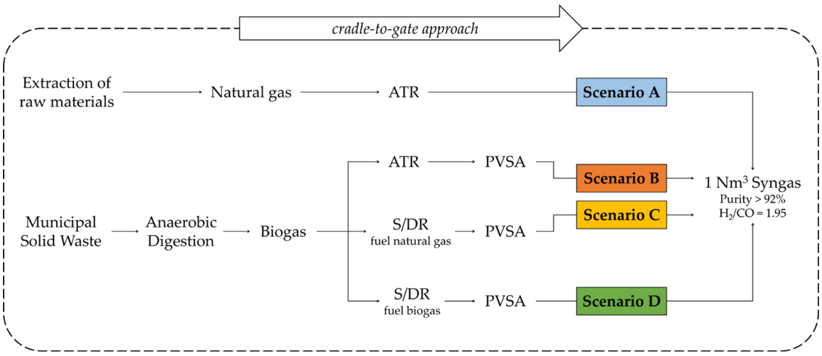


Figure 1 - Representation and system boundaries of the analysed scenarios.

[1] P. Weiland, *Appl. Microbiol. Biotechnol.* **2010**, *85*, 849−860.

[2] I. Angelidaki, L. Treu, P. Tsapekos, G. Luo, S. Campanaro, H. Wenzel, P. G. Kougias, *Biotechnol. Adv.* **2018**, *36*, 452−466.

[3] D. Andriani, A. Wresta, A., *Appl. Biochem. Biotechnol.* **2014**, *172*, 1909−1928.

Assessment of a sustainable biofilter technology for reducing the environmental spread of CECs and odour emissions

M. De Sanctis, S. Murgolo, G. Mascolo, V.G. Altieri, C. Di Iaconi

CNR, Istituto di Ricerca Sulle Acque, Via F. De Blasio, 5 – 70132 Bari

Treatment and disposal of excess sludge along with reduction of environmental spread of compounds of emerging concern (CECs) and odour emissions are three issues that commonly arise during sewage treatment in conventional wastewater treatment plants (WWTPs). It is worldwide recognized that municipal WWTPs are responsible for unpleasant odour emissions, and are not designed to completely remove a wide range of CECs released in the aquatic environment by domestic and industrial activities, as well as agricultural practices. Consequently, these contaminants (i.e. pharmaceuticals, personal care products, pesticides and industrial chemicals) are frequently detected at very low levels (ng/L to µg/L) in receiving water bodies and may have a strong impact not only on the environment but also on human health due to long-term exposure.

Moreover, sludge management currently represents one of the most challenging aspects in the field of wastewater treatment due to the large quantity produced and associated disposal problems.

The main goal of the present work was to investigate, for the first time, the effectiveness of an innovative plant design referred to as MULESL (*MUch LEss Sludge*, WO2019097463, with an already proven ability to reduce up to 80% the sludge quantity produced in the conventional WWTPs) in removing CECs and evaluating its impact on odour release from municipal WWTPs. The experimental campaign was performed in a municipal WWTP serving a small city located in Southern Italy (Putignano). MULESL plant performances were compared with those of the primary and secondary treatment stages of the conventional Putignano's WWTP treating the same municipal sewage and operating at a flow rate of 375 m^3/d and 3,600 m^3/d, respectively (Figure 1).

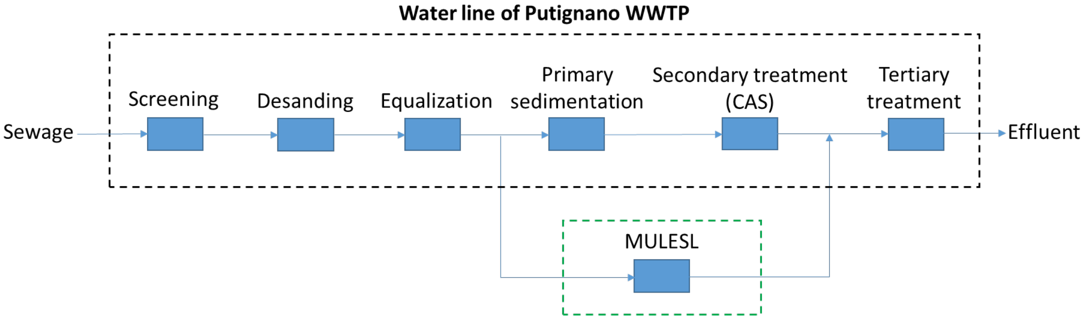


Figure 1. Sketch of the wastewater treatment line of both conventional and MULESL plant.

Results demonstrated that the MULESL plant was more effective than the conventional primary and secondary treatments in terms of CECs removal. In particular, it showed valuable removal efficiency against carbamazepine (55%), flecainide (59%) and clopidogrel (81%), which were not removed at all by the primary and secondary treatments of the conventional WWTP. This result was attributed to the high sludge retention time of the MULESL (enabling enrichment of slow-growing microorganisms), as well as to the biomass feature to grow in the form of biofilm and granules (favouring micropollutants absorption on biomass itself).

Odour impact analyses have shown that the MULESL plant was characterized by a much lower impact, i.e. 45% lower than that of primary and secondary treatments of the conventional WWTP.

Acknowledgment

This work was partially supported by the Italian National PON TARANTO Project (ARS01_00637) and MANGIAFANGHI project ("Sludge reducing during municipal wastewater) funded by Apulia region (Italy) within "Regional Technological clusters" call -FSC 2007/2013.

Vacuum-UV as pre- and post-treatment to biofiltration: a novel integrated treatment scheme for wastewater reuse

F. Piras[a], *S. Murgolo*[b], *G. Mascolo*[b], *K. Bell*[c] *G. Nakhla*[d], *G. Mele*[a], *D. Santoro*[d]

[a] *Department of Engineering for Innovation, University of Salento, Via Monteroni 73100, Lecce, Italy*
[b] *Water Research Institute, National Research Council (IRSA – CNR), via F. de Blasio 5, 70132, Bari, Italy*
[c] *Brown & Caldwell, 220 Athens Way #500, Nashville, TN, 37228, USA*
[d] *CBE Department, University of Western Ontario, London, Ontario, N6A 5B9, Canada*

In view of the increasing implementation of direct (DPR) and indirect (IPR) potable reuse as sustainable practices in water management, even in water-reach countries of the world, novel alternative technologies are requested to go beyond shortcomings deriving from membrane-based processes conventionally deployed in full scale drinking water treatment facilities.

Wastewater reclamation followed by advanced treatment prior to drinking water treatment has to ensure safety and reliability in removing not only conventional pollutants but also contaminants of emerging concern (CECs).

In this work, the vacuum UV-Based AOP (VUV), employing the irradiation at 185 nm to photolyze water molecules into HO•, has been tested as pre- and post-treatment to granular biofiltration at a laboratory scale. The novel treatment scheme was intended to work as a post-treatment of secondary treated municipal wastewater aiming at: i) understanding the impact of the AOP on biological removal of conventional contaminants and CECs, ii) providing a biofiltering stage to remove advanced oxidation by-products; iii) optimizing the removal of CECs.

The laboratory scale equipment consisted of 6 identical columns, three with granular activated carbon (GAC series), the other three with natural zeolite (GZ series) (Figure 1). 0.65 L/d of a secondary effluent (from Greenway WWTP in London Ontario) were treated in semi-batch operation with a HRT of 24 h. The VUV photo-reactor was equipped with a low pressure mercury vapor lamp and a proper quartz sleeve for monochromatic radiation at 185 nm. The reactor was connected to a 10 L recirculating tank. VUV doses were determined indirectly by fixing the electric energy consumption per unit treated volume, and two doses were chosen for pre-treatment and post-treatment, i.e. D1 and D2 corresponding to 1 kWh/m^3 and 10 kWh/m^3 respectively.

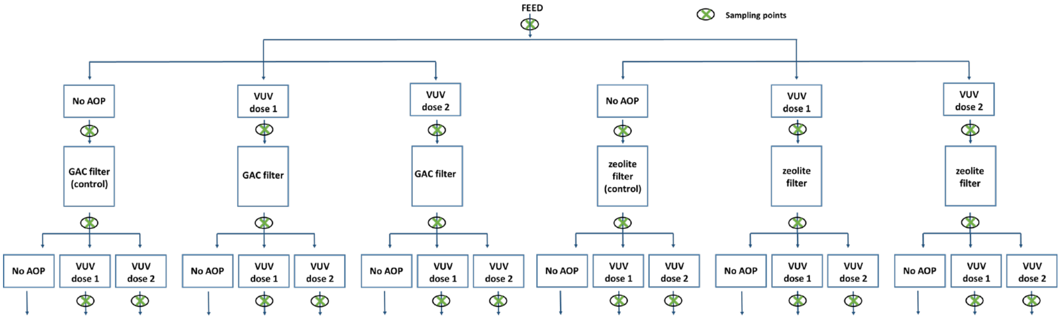


Figure 1. Operational conditions description

The performance of integrated treatment trains and the effect of VUV as pre- or post- treatment strategy for the removal of conventional water quality indicators of CECs was assessed. 29 CECs were detected and quantified by LC-HRMS with a targeted screening approach. Compared with zeolite, GAC was able to completely remove CECs while VUV as pre- and post-treatment exhibited an exponential abatement of the initial CECs load with increasing dose. In addition, VUV pre-treatment lead to an improvement in biodegradability of water matrix, favoring the removal of TOC in biofilters below 4 ppb in GAC columns.

The integration of VUV advanced oxidation with GAC biofiltration resulted in a promising treatment scheme as part of reaching potable water quality standards.

A study of the biocidal effectiveness of permaleic acid (PMA): new promising application in disinfection process

Concetta Pironti[a], Federica Dell'Annunziata[b], Rosa Giugliano[b], Veronica Folliero[b], Massimiliano Galdiero[b] , Maria Ricciardi[a], Gianluigi Franci[a], Oriana Motta[a], Antonio Proto[c]

[a]Department of Medicine Surgery and Dentistry, University of Salerno, via S. Allende, 84081 Baronissi (SA), Italy [b]Department of Experimental Medicine, University of Campania "Luigi Vanvitelli", Via S. Maria di Costantinopoli,16 80138 Naples, Italy [c]Department of Chemistry and Biology, University of Salerno, via Giovanni Paolo II, 132-84084 Fisciano (SA), Italy

The use of organic peracids in disinfection activities is increasingly attracting interest as a promising alternative to chlorine and chlorine-based agents. Chlorine products have some disadvantages, like the formation and accumulation of disinfection byproducts, the instability in the presence of organic matter, and the need for pH control[1]. Peroxide-based disinfectants are known to be environmental-friendly, broad-spectrum antimicrobial formulations, and sporicidal with applications in food, industrial areas, water treatments, medical devices, and synthetic chemical fields. In wastewater treatments and healthcare disinfection the most used and studied was the peracetic acid (PAA)[2]. Only recently, antimicrobial activity of permaleic acid (PMA) with respect to the growth inhibition of only *E. coli* in real tap water and wastewater was investigated, showing interesting results [3]. In this scenario, we evaluated a potential alternative to PAA: permaleic acid (PMA), a peroxycarboxylic acid produced from hydrogen peroxide and maleic anhydride.

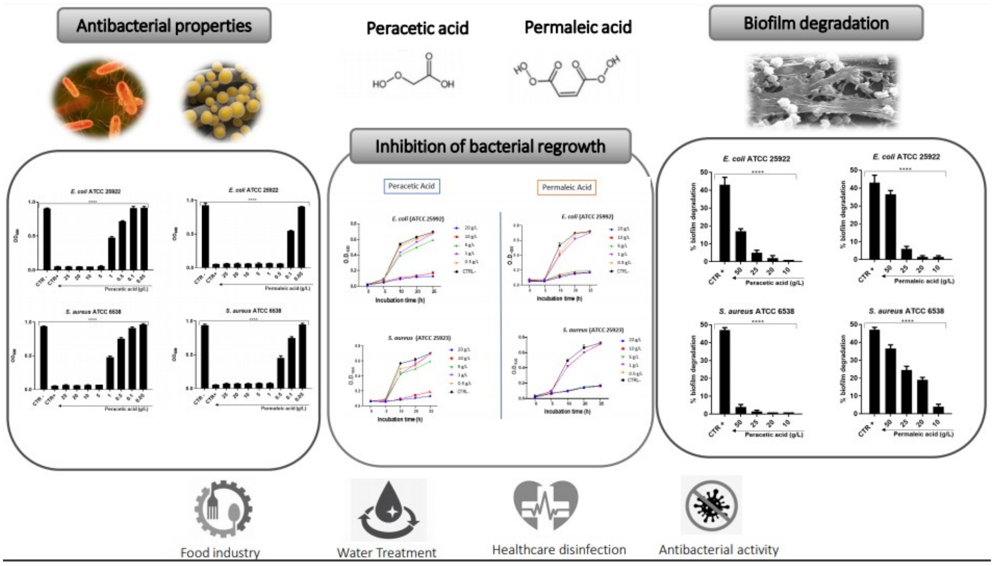


Figure 1. Comparison of PMA efficiency against PAA.

The present work concerns an innovative study on efficiency of permaleic acid (PMA) compared with peracetic (PAA) for its antimicrobial properties against *Escherichia coli* and *Staphylococcus aureus*. Disinfectant efficacy study was conducted using disk diffusion agar approach, broth microdilution method, and antibiofilm assays. This novel product (PMA) demonstrated an increase in the MIC value against *Escherichia coli* and *Staphylococcus aureus* respectively, compared to PAA, the best degradation effect on the biofilm matrix of both strains with PMA and the more efficiency of PMA to prevent the regrowth of planktonic cells of *Staphylococcus aureus* and

Escherichia coli. These results confirmed the possibility to use PMA as a valid alternative to the currently used disinfection methods.

[1] P., Ragazzo, N., Chiucchini, V., Piccolo, M., Spadolini, S., Carrer, F., Zanon, R., Gehr, *Water Res* **2020,** *184*, 116169.

[2] L., Domínguez Henao, A., Turolla, M., Antonelli, *Chemosphere* **2018**, *213*, 25–40. https://doi.org/10.1016/j.chemosphere.2018.09.005

[3] I., Zarrella, L., Falivene, V., Galiakberov, A., Fiorentino, R., Cucciniello, O., Motta, L., Rizzo, N., Krasnogorskaya, A. Proto, *Science of the Total Environment* **2021**, *767*, 144395.

2D Materials Engineered Membranes for a New Vision on Water Desalination

Annarosa Gugliuzza[a], Mirko Frappa[a], Giuseppe Di Luca[a], F. Macedonio[a],*
Enrico Drioli[a,b]

[a] Institute on Membrane Technology, CNR-ITM, Via P. Bucci Cubo 17/C, Rende (CS) Italy
[b]Department of Environmental and Chemical Engineering, University of Calabria, Via P. Bucci Cubo 44/A, Rende (CS) Italy
**corresponding author: a.gugliuzza@itm.cnr.it*

This work discloses the key role of 2D materials, including graphene and transition metal dichalcogenides (TMDs) compounds, in membrane operations designed to water desalination. 2D materials-enabled membranes are fabricated to work as active interfaces in membrane distillation (MD) and membrane crystallization (MCr) devices. Higher and energy saving production of fresh water together with recovery of better-quality crystals are obtained. Some experimental evidences suggest an involvement of 2D nanofillers in water transport mechanism. Chemisorption mechanisms at the vacancies of few layers materials are envisaged to accelerate water diffusion through the membranes, thus promoting higher fluxes and quicker nucleation and growth rate of crystals under supersaturation conditions. Also, a reduction of heat dissipation gives rise a subsequent enhanced thermal efficiency for the overall membrane distillation process.

Comparative analyses confirm improved chemistry-transport relationships, which can be regarded as a prelude to the development of new-concept nanocomposite membranes for fruitful water desalination through environment-friendly approaches. In this context, 2D materials engineered membranes show to be promising to travel successfully on the path to scaled up and eco-sustainable membrane distillation and membrane crystallization processes.

Acknowledgements

We acknowledge financial grant from ‘the Italian Ministry of Foreign Affairs and International Cooperation’ within the framework of the Great Relevance International Project Italy (MAECI)-China (NSFC) 2018-2021 - New Materials, with particular reference to Two-dimensional systems and Graphene (2DMEMPUR)

[1] M. Frappa, A.E. Del Rio Castillo, F Macedonio, A. Politano, E. Drioli, F. Bonaccorso, V. Pellegrini, A. Gugliuzza, *Nanoscale Adv.,* **2020**, *2*, 4728.
[2] ML Perrotta, F Macedonio, E Tocci, L Giorno, E Drioli, A Gugliuzza, *Environ. Sci.: Water Res. Tech.*, **2020**, *6*, 1723.
[3] E. Gontarek, F. Macedonio, F. Militano, L. Giorno M. Lieder, A. Politano, E. Drioli, A. Gugliuzza, *Nanoscale*, **2019**, *11*,11521.
[4] A. Gugliuzza, F. Macedonio, A. Politano, E. Drioli, *Chem. Eng. Trans*., **2019**, *73*, 265.
[5] F. Macedonio, A. Politano. E. Drioli. A. Gugliuzza, *Mater. Horiz.*, **2018**, *5*, 912.
[6] A. Gugliuzza, A. Politano, E. Drioli*, Curr. Opin. Chem. Eng.*, **2017**, *16*, 78.
[7] ML Perrotta, G Saielli, G Casella, F F. Macedonio, L Giorno, E Drioli, A. Gugliuzza, *Appl. Mater. Today* , **2017**, *9*, 1

Membrane biofunctionalization for pesticide removal in surface water and vegetative water

Giuseppe Vitola, Rosalinda Mazzei, Lidietta Giorno

National Research Council - Institute on Membrane Technology, CNR-ITM, Via P. Bucci Cubo 17/C, Rende (CS) Italy

The application of pesticides to support intensive agricultural activities inevitably leads to water, soil and vegetables pollution. Enzymatic detoxification of pesticides has become the subject of many studies because is an environmentally friendly method. The use of inherently resistant enzymes such as extremophiles and their immobilization on membranes can both ensure high activity and stability [1]. In the present work, a biocatalytic membrane reactor (BMR) was developed by using a thermophilic phosphotriesterase, an enzyme capable to hydrolyse organophosphate pesticides. The enzyme immobilization was carried out covalently by exploiting aldehyde groups created on purpose on three polymeric membranes. In particular, a hydrophobic membrane made of polyvinylidene fluoride (PVDF) and two hydrophilic membranes made of polyethersulfone coated with polyethyleneimine (PES-PEI) and regenerated cellulose (RC) were used. Surface modification of PVDF membrane was performed using 1,5-diamino-2-methylpentane (DAMP), under basic condition, as carrier of amino groups [2]. The amino groups of both PVDF-DAMP and PES-PEI membranes were reacted with an aqueous glutaraldehyde solution to graft aldehyde groups. The binding sites on the RC membrane were introduced by oxidizing the hydroxyl groups of the glucose units into aldehydes, which were subsequently derivatized with ethylenediamine. Afterward, the amino groups were reacted with glutaraldehyde. The obtained biocatalytic membranes where characterized by FT-IR, immunoelectron microscopy, static water contact angle, enzyme catalytic activity and stability. The regenerated cellulose membrane was selected to develop the BMR since the enzyme immobilized on this polymer showed the highest activity. Surface water and vegetative water (an agro-food industry effluent) were spiked with paraoxon and feed to the BMR as model streams to decontaminate. Enzyme loading and residence time influenced the paraoxon degradation degree. The conditions used with the developed system permitted to reach 89% and 70% degradation in surface water and in agriculture vegetative water, respectively. In both streams the enzyme immobilized on the membrane showed a deactivation constant about four-fold lower compared to the free enzyme. Kinetic studies demonstrated that the lower enzyme activity in vegetative water respect to surface water was due to competitive inhibition given by biophenols [3]. However, by using ionic surfactants enzyme activity was improved both in presence or in absence of inhibitor. Novel strategies to immobilize the enzyme within the membrane in presence of surfactant will be highlighted. The developed BMR represents a promising green alternative for environmental remediation.

[1] G. Vitola, R. Mazzei, T. Poerio, E. Porzio, G. Manco, I. Perrotta, F. Militano, L. Giorno, Biocatalytic membrane reactor development for organophosphates degradation, J. Hazard. Mater. **2019,** 365, 789-795.
[2] G. Vitola, R. Mazzei, E. Fontananova, L. Giorno, PVDF membrane biofunctionalization by chemical grafting, J. Membr. Sci. **2015**, 476, 483-489.
[3] G. Vitola, R. Mazzei, L. Giorno, Enzyme-loaded membrane reactor to degrade a pesticide in vegetative waters, J. Membr. Sci. **2021**, (accepted)

Protocol implementation of odour Proficiency Tests (PTs)

Domenico Cipriano[a]*, Amedeo M. Cefalì*[a,b]
[a] *RSE – Ricerca sul Sistema Energetico, Via Rubattino 54, 20131, Milan, Italy;*
[b] *University of Milano-Bicocca, Department of Earth and Environmental Sciences, Piazza della Scienza 1, 20126 Milan, Italy.*

In Europe, the odour concentration is determined by means of dynamic olfactometry, as standardized in EN 13725 [1]. Odour determination is subjected to uncertainty. Main important aspects are panel selection, measurement and sampling collection.

Aim of the present work is the evaluation to extent Proficiency Testing Schemes to odour measurements adding the presence of water and CO_2 at levels near real condition. In this first experiments was evaluated the possibility to create a synthetic atmosphere containing only n-butanol, N_2 and water vapour; to allow the generation of the high levels of butanol needed (up to 500ppm necessary prior the dilution into the bench), a vaporization system was realized and tested as gas cylinders are not available with such concentrations. Samples taken from the bench loop was analysed by using a GC–FID and by the means of olfactometric determinations, conducted using an olfactometer. In this work, a full-synthetic bench loop, based on controlled flow injections of known gases in a closed bench loop that allows the definition of the effluent gases and of the related reference values on metrological basis was used. The advantage of using this bench if the possibility of testing real samplings probes with values of humidity (up to 10% v/v), temperatures (between 60 and 180 °C) and gas matrix composition (CO_2, O_2 and other compounds) that, even if are not considered 'odourants' could alter the human perceptions and be considered as 'interferents'.

The samples were analysed both from a chemical and olfactometrical point of view, the results are shown in Table 1.

Table 1. Chemical and olfactometrical results.

Sample	C_{buOH} expected [ppm]	C_{buOH} measured [ppm]	C_{odour} expected [ouE/m^3]	C_{odour} measured [ouE/m^3]	Confidence interval
1	23.23	18.66	580	542	262-1084
2	40.67	36.81	1016	1085	543-2170
3	56.57	56.94	1414	1218	609-2436
4	74.36	69.52	1859	1934	495-1934
5	106.92	102.24	2673	2436	609-2436

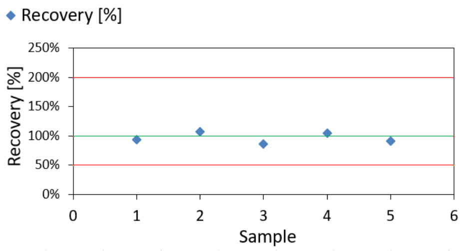


Figure 1. Recovery rates of measured values.

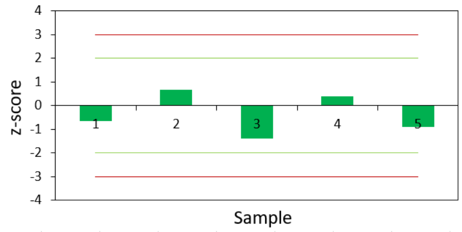


Figure 2. z-score values obtained.

Z-scores (Figure 1) and recovery rates (Figure 2) for each value were calculated. Data obtained showed variability of the values is in the range of 86% to 107% and allowed to verify that all the results can be considered acceptable as indicated in the standard EN 13725. In fact, in the tests carried out with this procedure, to generate an odorous sample with a known odor concentration was possible. An interesting future scenario would be the injection of interfering gases, e.g., different levels of H_2O, and CO_2, in the bench loop in order to evaluate the influence that the presence of those gases could have on the odour concentration measurement and int the stability process from samplig to analysis.

[1] CEN. EN13725, Air quality-Determination of odour concentration by dynamic olfactometry and odour emission rate from stationary by sources. **2004**.

Acknowledgments: This work has been financed by the Research Fund for the Italian Electrical System under the Contract Agreement between RSE S.p.A. and the Ministry of Economic Development - General Directorate for the Electricity Market, Renewable Energy and Energy Efficiency, Nuclear Energy in compliance with the Decree of March 8th, 2006.

Agar foam for the cleaning of art surfaces: a new approach

M. Anzani[a], A. Rabbolini[a], L. Toniolo[b], S.Goidanich[b], A. Sansonetti[c], P. Guzmán García Lascurain[b]

[a]Aconerre Conservation Studio, Milan, Italy
[b]Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, Milan, Italy
[c]Institute of Heritage Science, National Research Council (CNR), Milan, Italy

Cleaning works of art is a complicated task that requires a full comprehension of both the surface to clean and the soiling to be removed; this implies a critical choice of the cleaning methods and materials, the latter being the focus of the present work.

For the past years the usage of soft materials like gels, has allowed for a better control of the water release process onto the substrate, and the possibility for tunable materials that respond properly to each cleaning intervention [1,2]. However, many of the soft materials employed in the conservation science are synthetized in the laboratory increasing the time of preparation, cost, and potentially their chemical risk.

On the other hand, Agar gel –a natural polysaccharide harvested from algae– has been used to perform cleaning interventions of stone materials, gypsum works, and paintings, for the past years with positive results [3–5]. Agar gel presents the great advantage of being cheap, easily available, fast to produce and not toxic, which allows for easier conservation works.

One of the main advantages of Agar gel is its versatility, since it can adapt to the task at hand simply by changing the form of application: as viscous sol, a rigid gel, or in other forms. These possibilities have been studied in the past, especially in terms of the control of water release onto the substrate [6,7]. However, a new application form of Agar promises further control than the abovementioned, without compromising the existing benefits: Agar foam.

In the present study, a characterization of the Agar foam in terms of its structure, rheological properties, and water release performance is presented. The results obtained for the Agar foam are compared with the gel counterpart. With this, an efficiency assessment of this new application of Agar is obtained.

References:

[1] P. Baglioni, M. Baglioni, N. Bonelli, D. Chelazzi, R. Giorgi, Smart Soft Nanomaterials for Cleaning, in: G. Lazzara, R.F. Fakhrullin (Eds.), Nanotechnologies Nanomater. Diagnostic, Conserv. Restor. Cult. Herit., Elsevier, 2018: pp. 171–204.
[2] M. Bonini, S. Lenz, R. Giorgi, P. Baglioni, Nanomagnetic sponges for the cleaning of works of art, Langmuir. 23 (2007) 8681–8685. doi:10.1021/la701292d.
[3] M. Anzani, M. Berzioli, M. Cagna, E. Campani, A. Casoli, P. Cremonesi, M. Fratelli, A. Rabbolini, D. Riggiardi, Gel rigidi di agar per il trattamento di pulitura di manufatti in gesso, in: Quad. Cesmar7, 6, IL PRATO, Saonara, IT, 2008.
[4] M. Anzani, A. Rabbolini, Il Restauro di un Modello in Gesso: La "Ebe" di Antonio Canova, in: M. Fratelli, E. Signorini (Eds.), Probl. Conserv. Dei Manufatti Dell'Ottocento i Dipinti, La Cart. i Gessi; Atti, Probl. Di Restauro, Giornate Di Stud. Milano, 2-8-15-23-30 Maggio 2006, Spaz. Oberdan, Il Prato, 2008.
[5] D. Gulotta, D. Saviello, F. Gherardi, L. Toniolo, M. Anzani, A. Rabbolini, S. Goidanich, Setup of a sustainable indoor cleaning methodology for the sculpted stone surfaces of the Duomo of Milan, Herit. Sci. 2 (2014) 6.
[6] A. Sansonetti, M. Bertasa, C. Canevali, A. Rabbolini, M. Anzani, D. Scalarone, A review in using agar gels for cleaning art surfaces, J. Cult. Herit. (2020).
[7] M. Bertasa, C. Canevali, A. Sansonetti, M. Lazzari, M. Malandrino, R. Simonutti, D. Scalarone, An in-depth study on the agar gel effectiveness for built heritage cleaning, J. Cult. Herit. 47 (2021) 12–20. doi:10.1016/j.culher.2020.10.007.

Advanced systems for the cleaning of Cultural Heritage

Francesca Ramacciotti [a], Giorgia Sciutto [a], Silvia Prati [a], Chiara Gualandi [b], Maria Letizia Focarete [b], Rocco Mazzeo [a]

[a] Department of Chemistry ''G. Ciamician'', University of Bologna, Ravenna Campus, Via Guaccimanni 42, 48123 Ravenna, Italy; [b] Department of Chemistry ''G. Ciamician'', University of Bologna, Via Selmi 2, 40126, Bologna, Italy

Cleaning of cultural object is a particularly challenging operation which requires the selective removal of unwanted layers whose thickness is very limited in the range of few microns. Traditional chemical cleaning methods such as cotton swabs and poultices do not allow a controlled release of solvents, which may interact with inner paint layers, inducing degradation phenomena. To avoid this drawback chemical and physical gels have become popular for the removal of aged varnishes or coatings from artwork, as they exert a controlled superficial action.

Recently, our research group proposed poly-3-hydroxybutyrate (PHB)-based gels with green solvents as new cleaning systems for paintings and indoor bronzes [1,2].

To improve cleaning efficiency, solvent retention, handling, and mechanical properties the gels have been improved proposing sandwich-like composites in which the organogel (PHB + γ-valerolactone) is embedded in two external layers of electrospun nonwovens made of continuous submicrometric fibers produced by electrospinning. These new composites have been developed by using an organogel (PHB + γ-valerolactone) in the core and two external layers of electrospun nonwovens made of continuous submicrometric fibers produced by electrospinning. These new composites have proved to be extremely efficient in terms of cleaning as it was possible to completely eliminate the varnish layer with a minimal amount of solvent adsorbed by the painting layer after the treatment. Moreover, it has been demonstrated that the electrospun nonwoven layers act as mechanically reinforcement components, greatly improving the bending resistance of organogels and their handling [3].

Research efforts are currently aimed at testing different formulations for the removal of different undesired layers from cultural objects and at studying the mechanism of action of these new cleaning systems. Specifically, new cleaning systems have been tested not only for the removal of aged varnishes from paintings, but also for the selective elimination of vandalic graffiti from contemporary murals. The latter presents a new issue for conservator-restorer due to the similarities between the materials to be preserved and those to be removed.

The performances in terms of cleaning efficiency have been evaluated by applying an ad hoc analytical protocol.

(1) Prati, S.; Volpi, F.; Fontana, R.; Galletti, P.; Giorgini, L.; Mazzeo, R.; Mazzocchetti, L.; Samorì, C.; Sciutto, G.; Tagliavini, E. Pure and Applied Chemistry 2018, 90 (2), 239–251.

(2) Samorì, C.; Galletti, P.; Giorgini, L.; Mazzeo, R.; Mazzocchetti, L.; Prati, S.; Sciutto, G.; Volpi, F.; Tagliavini, E. ChemistrySelect 2016, 1 (15), 4502–4508.

(3) Jia, Y.; Sciutto, G.; Mazzeo, R.; Samorì, C.; Focarete, M. L.; Prati, S.; Gualandi, C. ACS Appl. Mater. Interfaces 2020, 12 (35), 39620–39629.

Evaluation of a new setup to improve the electro-kinetic desalination of porous materials in Cultural Heritage

R.Phaneuf[1], *M. Destefani*[2], *E.Balliana*[2], *F.C.Izzo*[2], *L.Falchi*[2], *P Lucero-Gomez*[2], *D.Cimino*[2], *E.Zendri*[2]

[1] *Dept. Materials Science and Engineering, University of Maryland, College Park, USA;* [2]*Dept. of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Mestre (VE)*

Rising damp, i.e. capillary rise of water from the ground to the walls of a building, is a well-known phenomenon in ancient buildings and one of the most recurrent hazards to monuments, along with marine aerosol deposition on buildings surfaces. Remediation or mitigation of salt weathering is a major challenge, and the common strategy to preserve cultural heritage from soluble salts is to remove them or reduce their presence. For this pourpose, dry and/or aqueous methods, as the use of clay/cellulose poultices, could be useful. The application of poultices is not risk-free and in some cases, this intervention seems to be more dangerous than leaving soluble salts in the material (1). In addition, the application of poultices has several disadvantages such as the low efficiency of extraction in depth, the slowness of the extraction process, and the high influence that the properties of the poultices and rocks have in the efficiency of the technique. Recently accelerated desalination by an electro-kinetic approach has been proposed, aiming to remove ionic species using an externally applied electric field (2). One of the particularly relevant disadvantages in the application of this desalination method is the possibility of chemical alteration of carbonatic materials (stone, mortars, plasters) because of extreme pH values (acid and alkaline) generated during the electro-kinetic treatment near the electrodes due to the water hydrolysis (3). This disadvantage recently has been greatly reduced by the introduction of a buffer solution and adding $CaCO_3$ to the poultices, in order to neutralize the acid components at the anode (4). This research proposes a "DAC-S" (a Double Anode and Cathode setup) geometry for the case in which the object can be surrounded by an electrically conductive water-saturated poultice. The efficacy of the new setup has been evaluated on brick samples and Lecce stone (calcareous porous matrix) treated with a saturated solution of sodium chloride, the most commonly present salt in artworks and masonries in coastal areas. The amount of salt extracted by the samples has been measured by conductivity methods after and before the electro-kinetic desalination, in order to evaluate the effectiveness of the methodology. The pH in the region of the anode and near the sample has been monitored during the extraction. The application of the electro-kinetic method developed in this research will constitute an important innovation in the conservation of the cultural artifacts and historical masonries subjected to the degradative action of the soluble salts.

[1] Bosch-Roig, P.; Allegue, H.; Bosch, I., Sustainability, 2019, 11, 4227. https://doi.org/10.3390/su11154227
[2] Moghadam, M.J., Moayedi, H., Sadeghi, M.M. et al., Environ. Geochem. Health 38, 1217–1227,2016, https://doi.org/10.1007/s10653-016-9795-3)
[3] Auras, M; Poultices and mortars for salt contaminated masonry and stone objects, in Proceedings of the International Conference on Salt Weathering on Buildings and Stone Sculptures, 2008, 197–217, Copenhagen, Denmark
[4] Feijoo, J.; Rivas, T.; Nóvoa, X.R.; Ottosen, L.M., International Journal of Architectural Heritage, 2020, 14:5, 678-693, DOI: 10.1080/15583058.2018.1561962

Deep Eutectic Solvents (DES) based on choline chloride and betaine for cleaning gelatin residues from cellulose nitrate cinematographic films.

Marco Valente Chavez Lozano [a], *Giorgia Sciutto*[a], *Silvia Prati*[a], *Rocco Mazzeo*[a]

[a] *University of Bologna, Department of Chemistry "G. Ciamician", Ravenna Campus, Via Guaccimanni, 42–48121, Ravenna, Italy*

Historical photographic negatives and cinematographic films with cellulose nitrate (CN) supports are known to be intrinsically unstable, showing deterioration mechanisms related to the thermal, photocatalytic and hydrolytic loss of nitro substitutive groups from the CN chain. To prevent the disappearance of this heritage, its scanning and digitalization becomes a priority.

However, softened emulsion residues often hinder the scanning of CN films which have already undergone some degradation. Such residues are mainly composed of alkaline photographic gelatin, whose viscosity decreases when the pH falls below the isoelectric point of gelatin, and when its molecular weight decreases due to hydrolysis reactions promoted by NO_2 emissions.[1–3]

Traditional approaches to clean gelatin residues from the surface of CN bases and from the sides of film rolls include mechanical removal with scalpels and the use of polar solvents; but these methods are either slow, ineffective or could potentially damage the degraded CN support and the remaining gelatin emulsion at the other side of the film.

Accordingly, we have evaluated the performance of three Deep Eutectic Solvent (DES) formulations when applied for CN cinematographic film cleaning. These DES have been previously proposed for the extraction of proteinaceous material[4,5], but their use for the restoration of photographic negatives or cinematographic films has not been reported yet.

We synthesized the DES by mixing choline chloride with ethylene glycol, betaine with ethylene glycol and betaine with urea at a 1:2 molar ratio, adding 10%wt and 30%wt water respectively to each betaine-based DES. These mixtures are unexpensive, easy to prepare, green (nonvolatile, safe towards operator and the environment), and non flammable.

Selected areas over frames of a real deteriorated CN cinematographic film were cleaned from gelatin accretions with a cotton swab dipped in DES, employing isopropyl alcohol to remove the remaining DES residues.
To evaluate the cleaning performance, each area was characterized and documented before and after treatment using high-resolution Optical Microscopy in Bright and Dark Fields, µATR-FTIR and cross-section observation under visible and UV light.

All treatments proved effective for the removal of gelatin residues and harmless towards CN film supports at selected application times, showing superior cleaning power compared to traditional methods, thus being suitable for cinematographic and photographic film restoration.

[1] FilmCare.org, https://www.filmcare.org/vd_binder.php (accessed Apr 30, 2021).
[2] G. M. Haist, *Modern Photographic Processing*; Wiley, 1979.
[3] T.-P. Nguyen, B. Lavédrine, F. Flieder, *The Imaging Science Journal* **1997**, *45* (3–4), 239–243.
[4] C. Bai, Q. Wei, X. Ren, *ACS Sustainable Chem. Eng.* **2017**, *5* (8), 7220–7227.
[5] N. Li, Y. Wang, K. Xu, Y. Huang, Q. Wen, X. Ding, *Talanta* **2016**, *152*, 23–32.

Halloysite nanotubes: a versatile material for conservation of cultural heritage

Lorenzo Lisuzzo, Giuseppe Cavallaro, Stefana Milioto, Giuseppe Lazzara
Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze, pad. 17, 90128 Palermo, Italy. giuseppe.lazzara@unipa.it

In the last years, innovative strategies based on clay nanoparticles have been proposed for conservation of cultural heritages, including the consolidation/protection of lignocellulosic materials as well as the protective coating/cleaning of solid surfaces. Among the nanoclays, halloysite nanotubes are promising[1,2,3] because of their hollow tubular shape, tunable interface chemistry and high specific surface. Here, we investigated the efficiency of hybrid materials based on halloysite as protective consolidants of waterlogged archeological woods as well as cleaners for solid substrates.

In consolidation and protection, the main perspectives are devoted at obtaining nanomaterials with smart performances and stimuli responsive features. These characteristics are strategic in many aspects of conservation of cultural heritages such as controlled cleaning or development of smart protective coatings and active consolidants. The use of nanotubular clays put forward new sustainable strategies removing the cost barrier typical of nanotecnologies. In case of coating or protective additives, nanoclays are proposed as nanocontainers for active species to generate a time-extension in the efficacy of the treatment.

[1] Cavallaro, G.; Milioto, S.; Lazzara, G. Halloysite Nanotubes: Interfacial Properties and Applications in Cultural Heritage. Langmuir 2020, 36, 3677–3689, doi:10.1021/acs.langmuir.0c00573.
[2] Lisuzzo, L.; Hueckel, T.; Cavallaro, G.; Sacanna, S.; Lazzara, G. Pickering Emulsions Based on Wax and Halloysite Nanotubes: An Ecofriendly Protocol for the Treatment of Archeological Woods. ACS Appl. Mater. Interfaces 2021, 13, 1651–1661, doi:10.1021/acsami.0c20443.
[3] Cavallaro, G.; Milioto, S.; Nigamatzyanova, L.; Akhatova, F.; Fakhrullin, R.F.; Lazzara, G. Pickering Emulsion Gels Based on Halloysite Nanotubes and Ionic Biopolymers: Properties and Cleaning Action on Marble Surface. ACS Appl. Nano Mater. 2019, doi:10.1021/acsanm.9b00487.

CAPuS project: research and higher education allied for the Conservation of Art in Public Spaces

D. Scalarone

[a] *Department of Chemistry, University of Turin, Via Pietro Giuria 7, 10125 Turin (Italy)*

Conservation of Art in Public Spaces (CAPuS) project was co-funded by the European Commission under the Erasmus + Knowledge Alliances Programme. The consortium is composed of 17 partners from 5 European countries, and includes universities, companies, research centres, an NGO, a museum and 3 municipalities. The project, launched in 2018, started from the evidence that there was a lack of specific initiatives for the conservation of street and urban art, nor was this topic present in academic programmes. During the three years of the project, through the close collaboration of researchers, teachers, conservators and entrepreneurs, research and training activities have been carried out aimed at two main results: the development of guidelines for the conservation of contemporary works of art belonging to street and urban art, and the definition of a teaching module and an e-learning module to prepare present and future conservators to face the problems and specificities of conservation interventions on works of art in public spaces.
The project featured four main steps:
1) the selection of case studies, interviews with artists and the creation of a digital repository of the artworks studied within CAPuS, including general information, photo documentation, condition and laboratory reports and archival documents;
2) the identification and analytical characterization of the constituent materials and decay processes;
3) the testing of products and conservation treatments;
4) the definition of conservation guidelines for product selection, on-site treatment evaluation, preventive conservation and maintenance;
5) the definition of a teaching module addressed to lecturers and a e-learning module addressed to university students or experts in conservation who want to deepen their knowledge and understanding of the problems and specificities of conservation interventions on complex public art works, especially murals and painted metal sculptures.

This contribution aims to give an overview of the activities and results of the project focusing on those most closely related to chemistry: 1) the diagnostic campaign, carried out using non-invasive and micro-invasive techniques, 2) the studies aimed at understanding the ageing processes of the painting materials used in street art and their effects on the state of conservation of the artworks, 3) the analytical protocol followed to evaluate the effectiveness and selectivity of the cleaning methods investigated to remove signs of graphic vandalism. The results of all these phases of the research, together with the aspects more related to conservation, the socio-cultural context, the role and involvement of stakeholders, are the basis of the innovative and multidisciplinary e-learning module now hosted in the e-learning platform of the University of Turin.

[1] CAPuS Digital Repository, http://repository.capusproject.eu/
[2] M. Bertasa, C. Ricci, A. Scarcella, F. Zenucchin, G. Pellis, P. Croveri, D. Scalarone, *Coatings* **2020**, *10*, 1019.

Evaluation of the effectiveness of coatings for the protection of outdoor terracotta artworks through artificial ageing

S. Spadavecchia[a], C. Velino[b], C. Chiavari[a], S. Gualtieri[c], A.C. Hillar[a], E. Bernardi[b].

[a]*Dipartimento di Beni Culturali, Università di Bologna;*
[b]*Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, elena.bernardi@unibo.it*
[c]*CNR-ISTEC Istituto di Scienza e Tecnologia dei Materiali Ceramici.*

Outdoor historical-artistic heritage is increasingly exposed to risks related to climate change and air pollution, which in the future will contribute to further accelerate the phenomena of deterioration [1]. Unlike museum collections, it is difficult to control or limit the parameters that are crucial for the protection of an object when it is exposed outdoors. Therefore, one of the adoptable strategies consists in the direct intervention on the work of art, through the interposition of a 'barrier', such as a protective or a surface treatment, that could mitigate the effect of external agents.

The aim of this research is to study new materials suitable for the conservation and restoration of outdoor terracotta artworks, a field that today has very few comparisons and bibliographic references, compared to other materials.

Starting from the conservative study and the restoration of a terracotta sculpture of the Open Air Museum of Faenza, the Wind Wall by Domenico Matteucci, an experimental investigation has been carried out in order to evaluate the effectiveness, for terracotta artworks, of some protective coatings available on the market. Four coatings were selected and assessed according to their compatibility with the terracotta substrate and resistance to the main degradation agents.

The selected coatings (vinylidene-fluoride-hexafluoropropene copolymer at 3% in acetone, aqueous emulsion of alkylpolysiloxane, aqueous dispersion of functionalized silica nanoparticles, nanostructured and functionalized silica gel in hydroalcoholic solution) were applied by brush on carbonate terracotta samples fired at a temperature of 980°C.

Subsequently, the specimens were subjected to accelerated aging, which included a run-off test with acid rain [2] and a climate chamber test with exposure to UVA radiation [3]. These tests were properly set-up to investigate the interaction mechanisms between the environment and the ceramic substrate, separately highlighting the effects of heavy rain and daily variation of temperature, relative humidity and irradiation.

The effectiveness of the treatments was evaluated through colorimetric analyses, water absorption capacity measurements, attenuated total reflectance infrared spectroscopy (FTIR-ATR), mercury intrusion porosimetry (PIM) and assessment of the amount of calcium ions brought into solution by rain through atomic absorption spectroscopy (AAS).

On the basis of the results obtained, the performance of the coatings was evaluated and compared.

[1] Global Climate Change on Built Heritage and Cultural Landscapes-The Noa's Ark project, Atlas and Guidelines, **2007**, https://cordis.europa.eu/project/id/501837/it

[2] E. Bernardi, C. Chiavari, B. Lenza, C. Martini, L. Morselli, F. Ospitali, L. Robbiola, *The atmospheric corrosion of quaternary bronzes: The leaching action of acid rain,* Corrosion Science **2009**, *51*, 159-170, doi: https://doi.org/10.1016/j.corsci.2008.10.008

[3] C. Chiavari, A. Balbo, E. Bernardi, C. Martini, F. Zanotto, I. Vassura, M.C. Bignozzi, C. Monticelli, *Organosilane coatings applied on bronze: influence on UV radiation and thermal cycles on the protectiveness*, Progress in Organic Coatings **2005**, *82*, 91-100, doi: https://doi.org/10.1016/j.porgcoat.2015.01.017

Integrating biodegradation and ozone-catalysed oxidation for treatment of biomass gasification wastewater

D. Sgherza[a], S. Pentassuglia[a], V.G. Altieri[a], G. Mascolo[a], M. De Sanctis[a], C. Di Iaconi[a]

[a] *CNR, Istituto di Ricerca Sulle Acque, Via F. De Blasio, 5 – 70132 Bari, Italy.*

Syngas purification via wet-scrubbing processes generates a relevant amount of wastewater, which requires proper treatments before its disposal or reuse. Integrating chemical with cost-saving biological approaches represent a valuable alternative to traditional chemical-physical treatments. This study investigated the effectiveness of the BIO&CHEM treatment scheme for the treatment and reuse of wastewater collected from a wet-scrubber unit (chemical oxygen demand, COD = 2600 mg/L) containing several hazardous pollutants such as phenol (110 mg/L), xylene (64 mg/L) toluene (25 mg/L) and benzene (5 mg/L). The BIO&CHEM system included a sequencing batch biofilter granular reactor (SBBGR) and an ozonation unit that were operated at different hydraulic retention times (HRTs, from 5 to 1 day) and transferred ozone doses (TODs, from 400 to 250 mg/L_{inf}), respectively. As shown in Fig. 1, when a 4 d-HRT was selected, biologically treated wastewater was characterized by a COD of 140 mg/L and its toxicity on *Daphnia magna* was decreased from 100% to 5%. Fig. 1 also highlights the integration between the biological SBBGR-based treatment (HRT=1.5 d) and the ozone-catalysed oxidation (TOD = 280 mg/L_{inf}) lowered effluent COD to 33 mg/L and erased toxicity on *Daphnia magna*. Furthermore, the investigated aromatic and polyaromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs; including benzene, toluene, xylene and phenol, see Fig. 2) were completely removed. The analysis of the reactor biomass, performed at the end of the experimental trial, excluded also their mere accumulation within the reactor due to absorption or adsorption on the sludge.

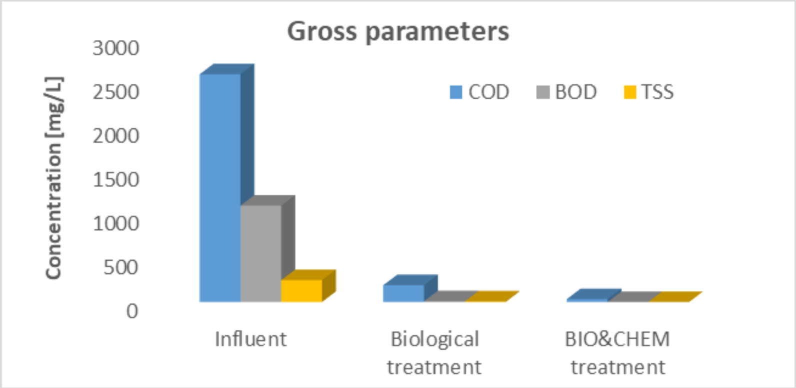


Fig. 1. Some of the main gross parameters monitored during the experimental campaign.

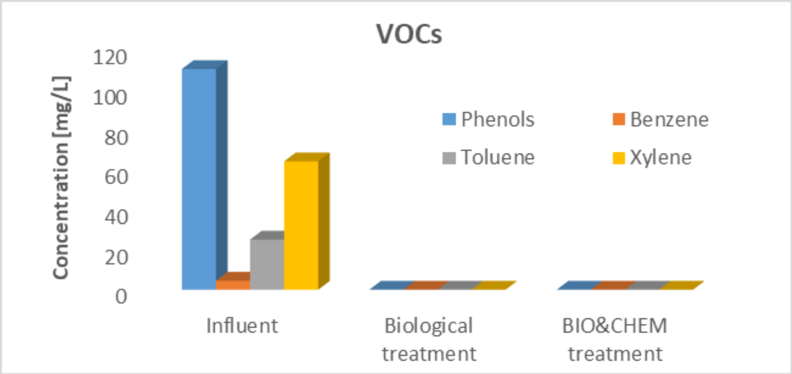


Fig. 2. Trend of the studied VOCs concentration according to the undergone treatment.

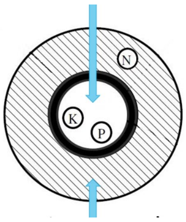
An integrated system for a new controlled release fertilizer based on lightweight ceramic aggregates starting from waste materials and bio-products

Francesco Barbieri[b], Claudia Righi[a], Fernanda Andreola[a], Isabella Lancellotti[a], Lara Maistrello[c], Monia Montorsi[b], Alessandro Bertacchini[b], Giovanni Verzellesi[b], Elisabetta Sgarbi[c], Luisa Barbieri[a]

[a] *Dipartimento di Ingegneria "Enzo Ferrari", Università degli Studi di Modena e Reggio Emilia, Modena*
[b] *Dipartimento di Scienze e Metodi dell'Ingegneria, Università degli Studi di Modena e Reggio Emilia, Reggio Emilia*
[c] *Dipartimento di Scienze della Vita, Università degli Studi di Modena e Reggio Emilia, Reggio Emilia*

A controlled release fertilizer is a granulated fertilizer that releases nutrients gradually into the soil within a long period. The formulations are often based on nitrogen-phosphorous-potassium (NPK) with, eventually, secondary nutrients like calcium and magnesium compounds. Usually these formulations include nutrients in granular form, which are encapsulated by a special biodegradable polymeric membrane. This work proposes granular materials with a core-shell structure in which an aluminosilicate and/or silicate matrix is coated with organic matter. All core nutrients derive from agro-food and post-consumer residues, thus fitting into a circular economy perspective [1]. The specific residues used to develop the core-shell aggregate lead to: i) a functionalized product characterized by high porosity typical of a lightweight material; ii) enrichment of the PK-based inorganic fraction (as received or previously vitrified); iii) enrichment in N deriving from the organic fraction. Application fields for these aggregates include vertical woods, green roofs, hydroponic and indoor crops, where besides density, porosity, water absorption, pH, conductivity, it is also important to monitor nutrients and micro-pollutants in different environments with calibrated lighting systems. A specific indoor horticulture system has been set up, using these aggregates and LED lights, as they can improve seed germination and plant growth in indoor applications. DoE methodology was used to analyze data and minimize the number of empirical tests. So far, the achieved results are encouraging and indicate:

i) release of the P and K macronutrients regulated both by the glass structure and by the nitrogen coating;
ii) absence of micro-pollutants release;
iii) a synergic positive interaction between the new materials and the LED modules, which lead to improved plant growth [2].



[1] S. Barbi, F. Barbieri, F. Andreola, I. Lancellotti, C. Martínez García, T. Cotes Palomino, M. Montorsi, L. Barbieri, *Env. Eng & Manag. J.*, **2020**, *19[10]*, 1669.

[2] S. Barbi, F. Barbieri, A. Bertacchini, L. Barbieri, M. Montorsi, *Appl. Sci.* **2021**, *11*, 2497. https://doi.org/10.3390/app11062497

Reutilization of residues from municipal wastes pyrolysis to improve and regenerate asphalts

Pietro Calandra[a], *Paolino Caputo*[b], *Michela Alfè*[c], *Valentina Gargiulo*[c], *Renata Migliaccio*[c], *Valeria Loise*[b], *Michele Porto*[b], *Cesare Oliviero Rossi*[b]

[a] *CNR-ISMN, Via Salaria km 29.300, 00015, Monterotondo Stazione (RM), Italy;* [b] *Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 14/D, Rende (CS), 87036, Italy & UdR INSTM della Calabria Affiliation (Times New Roman, 11 pt, Italics, justified)* [c]*Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS-CNR)*

We identified the physico-chemical principles at the basis of the lifetime prolonging in aged asphalts in road pavements, as well as of their eventual regeneration when, due to usage conditions, they lose the required characteristics [1]. We have therefore individuated some substances which can be used as additives to prolong the asphalts lifetime and to regenerate them, when aged, avoiding landfilling and limiting the production of new ones. In the optics of circular economy, we are planning to use the residues deriving from pyrolysis implants, which eliminate municipal wastes without significantly impacting on CO_2 emission, producing however, a non negligible amount of liquid (bio-fuel) and solid (char) residues, of difficult re-utilization [2].

It is possible, therefore, to re-use the residues coming from pyrolysis implants to produce better and longer lifetime asphalts and to regenerate them in-loco when aged.

This would harmonize the cycles of urban wastes and of asphalts, closing them without any further CO_2 emissions

[1] V. Loise, P. Caputo, M. Porto, P. Calandra, R. Angelico, C. Oliviero Rossi, *Appl. Sci.* **2019**, *9*, 4316.

[2] A.T. Sipra, N. Gao, H. Sarwar, *Fuel Processing Technology*, **2018**, *175*, 131

Exposure modelling of emerging contaminants in the Venice lagoon - a case-study on active pharmaceutical ingredients

Calgaro L.[a], Giubilato E.[a], Lamon L.[a], Marchese E.[a], Calore F.[a], Semenzin E.[a], Marcomini A.[a]*

[a]*University Ca' Foscari Venice, Dept. of Environmental Sciences, Informatics and Statistics, Via delle Industrie 21/8 30175 Marghera, Venice (Italy)*

Active pharmaceutical ingredients are used for the treatment of diseases both in humans and animals but, at the same time, there is evidence of risks to the environment and to human health caused by the release into the environment of these chemicals during their manufacture, use and disposal. In particular, traditional technologies for wastewater treatment have shown to be less effective for several of these substances, thus posing risks to the receiving waterbodies.

Furthermore, since monitoring programmes to investigate the presence of several pharmaceutical compounds of emerging concern in the environment have been implemented only in the last few years there is a lack of historical trends, but the use of predictive exposure models has been identified as a complementary, low-cost tool to support both the investigation of behaviour and environmental fate of these contaminants and the assessment of associated risks.

The lagoon of Venice, a highly valuable coastal transition environment surrounded by a densely populated area, is potentially subject to pharmaceutical contamination due to wastewater discharges from both Venice historical city centre, and from its drainage basin. In this context, there is still a lack of information on the presence of pharmaceuticals in both water and sediment compartments despite various water quality monitoring programs conducted in accordance with the Water Framework Directive (DIR 2000/60/CE) and other regional and national regulations.

The aims of this work, developed within the Venezia2021 project, are: (i) to provide an emission inventory of several active pharmaceutical ingredients in the study area, (ii) to investigate the environmental distribution and fate of these chemicals in the lagoon of Venice, with particular attention to the processes involved in their natural attenuation, and (iii) to define a risk-based priority list of contaminants specific to the case study area, taking into consideration the overall mass balance of the pollutants.

Pharmaceutical sales data for human consumption obtained from the Veneto Region Authority, census and geographical information were integrated through statistical data treatment and GIS-based spatial analysis to develop an emission inventory. In addition, a multimedia level III fugacity model was applied and evaluated to carry out an exposure assessment of these chemicals for the lagoon of Venice. Model evaluation was carried out by performing uncertainty and sensitivity analysis on the predicted results, as well as by comparing concentrations calculated by the model after calibration with the concentrations measured in lagoon water and sediments samples taken during two recent sampling campaigns (2019).

Modelling eutrophication processes in the Venice Lagoon: a multivariate Machine Learning approach

Zennaro F. [a,b], *Furlan E.*[a,b], *Aslan S.*[a], *Critto A.*[a,b], *Marcomini A.*[a,b]

[a] *Department of Environmental Sciences, Informatics and Statistics, University Ca' Foscari Venice, Italy;*
[b] *Centro-Euro Mediterraneo sui Cambiamenti Climatici (CMCC), Lecce, Italy.*

Eutrophication is a worldwide environmental problem affecting the health of close and semi-close water bodies as lagoons, lakes, and estuaries. The ecological and environmental state of water ecosystems is increasingly threatened by cultural eutrophication, i.e. the excessive plant growth resulting from nutrient enrichment due to human activities (e.g., urban and agricultural waste and runoff), a process further exacerbated by simultaneous changes in water temperature, and turbidity. A multivariate approach is then required to understand and model spatio-temporal changes in water quality, accounting for the complex interactions among natural and human-made pressures.

To this aim, a machine learning-based Long short-term memory (LSTM) algorithm integrating ecological, chemical, and physical data, was applied in this study to model Chl-a concentration, used as a proxy indicator of eutrophication processes in the Venice Lagoon case study. Specifically, half-hourly water quality (e.g., OD, salinity, and turbidity) and hydro-meteorological data (e.g., precipitation and river flow) for the 2008-2019 timeframe were used to train, validate and test the LSTM models developed for each of the 7 monitored lagoon water bodies.

Results from the case study showed as the LSTM model successfully captured Chl-a trends under a multivariate perspective accounting for changes in multiple concurrent parameters. In particular, models developed for water bodies with few missing data showed very good performances with also high capability to capture Chl-a extreme low and high values.

The proposed Machine Learning-based multivariate model represents a valuable approach to strengthen eutrophication modelling and management, which could be a significant advantage for the design of effective strategies aimed at preventing transitional ecosystems' deterioration. Moreover, the designed model is a promising tool, ready for *'what-if'* scenario analysis accounting for changes in climate conditions and urban development.

Bioaerosol detection, pathogen airborne transmission and abatement studies: capacity building, experimental results and perspectives from the COVID-19 pandemic

Pierluigi Barbieri[a,b], Sabina Licen[a,b], Lorenzo Martello[a,b], Massimo Borelli[a], Sabrina Semeraro[b], Anna Lilian Gardossi[f], Gianluigi de Gennaro[c], Jolanda Palmisani[c], Alessia di Gilio[c], Maria Grazia Perrone[d], Marco Zonca[d], Prisco Piscitelli[e], Alessandro Miani[e,f], Francesca Malfatti[g], Valentina Torboli[g], Alberto Pallavicini[g], Luisa Zupin[h], Sergio Crovella[i], Francesco Fontana[l], Maurizio Ruscio[m]

[a] *Dept. of Chemical & Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127, Trieste, Italy*
[b] *INSTM National Interuniversity Consortium of Materials Science and Technology, Via G. Giusti, 9 50121, Firenze, Italy*
[c] *Dept. of Biology, University of Bari "Aldo Moro", Via Via E. Orabona, 4 70124, Bari, Italy*
[d] *Environmental Research Division, TCR TECORA, Via delle Primule, 16 Cogliate (MB), I-20815 Italy*
[e] *Italian Society of Environmental Medicine (SIMA), Corso di Porta Vercellina 9, Milano,20149 Italy*
[f] *Dept. of Environmental Science and Policy, University of Milan, Via Celoria 2,20133 Milano Italy*
[g] *Dept. of Life Sciences, University of Trieste, Via L. Giorgieri 8, 34127, Trieste, Italy*
[h] *Institute for Maternal and Child Health, IRCCS Burlo Garofolo, Via Dell'Istria 65/1, 34137, Trieste, Italy*
[i] *Dept. Biological and Environmental Sciences, University of Qatar, Doha, 2713, Qatar*
[l] *Azienda Sanitaria Universitaria Giuliano Isontina – Ospedale San Polo Via L. Galvani 1, 34074, Monfalcone (GO), Italy*
[m] *Azienda Sanitaria Universitaria Giuliano Isontina – Ospedale Maggiore Piazza Dell'Ospitale 1, 34129, Trieste (TS), Italy*

Stress stimulates reaction and adaptation in living organisms and the COVID 19 pandemic activated a reorganization, coordination and refocalization in research groups. We report about activities on the search of SARS-CoV-2 RNA from outdoor [1] and indoor [2] air particulate matter, studies on stability of RNA during PM sampling on filters, infectivity assessment of environmental samples and the setup of BSL3 and BSL2 laboratories for technology testing. Quantification of UV and photocatalytic abatement of airborne viruses requires viable bioaerosol generation and sampling preserving infectivity. Aerosolization of bacteria (for assessment of chirurgical masks Bacterial Filtration Efficiency – EN14683:2019) and viruses by medical therapy nebulizer, Blaustein Atomizing Module (BLAM) and prototype devices will be compared, as well as viable aerosol sampling by impinger tailored for bioaerosol collection (SKC Biosampler; high viable aerosol collection efficiency for particles 300 nm or greater) and by Laminar flow Growth Tube Collector [3] (VIVAS BioSpot sampler; high viable aerosol collection efficiency for particles 10 nm or greater). This last recent technology opens a window on viable bioaerosol of size smaller than 300 nm that till now has been locked. Design for testing airborne microorganisms technological abatement in safe conditions will be also commented.

[1] L. Setti, F. Passarini, G. De Gennaro, P. Barbieri, M.G. Perrone, M. Borelli, J. Palmisani, A. Di Gilio, V. Torboli, F., Fontana, L. Clemente, A Pallavicini, M., Ruscio, P. Piscitelli, A. Miani, 2020. Environ. Res. 188, 109754. https://doi.org/10.1016/j.envres.2020.109754.
[2] P. Barbieri, L. Zupin S. Licen V. Torboli, S. Semeraro, S. Cozzutto, J. Palmisani, A. Di Gilio, G. de Gennaro, F. Fontana, C. Omiciuolo, A. Pallavicini A, M. Ruscio, S. Crovella. Environ Res. 2021 Apr 24;198:111200. doi: 10.1016/j.envres.2021.111200.
[3] J.A. Lednicky, M. Pan, J. Loeb, H. Hsieh, A. EigurenFernandez, H. Hering, Z.H. Fan, C.Y. Wu, 2016. Aerosol. Sci. Technol. 50 (7), i–iv. https://doi.org/10.1080/02786826.2016.1179254.

Evaluation of PM_x chemical composition and planning of a vegetable-green barrier in a high traffic site in Milan

A.M. Cefalì[a], L. Ferrero[a], A. Bigogno[a], N. Losi[a], L. Scibetta[a], M. Lapi[b], A. Ballarin Denti[b],

G. Rabotti[b] and E. Bolzacchini[a]

[a] Department of Earth and Environmental Sciences, University of Milano-Bicocca, Milan, 20126, Italy;
[b] Lombardy Foundation for the Environment, Seveso (MB), 20822, Italy

Air quality is particularly polluted in urban areas due to of the high level of emissions by anthropogenic activities and related secondary formation. Traffic-related air contaminants are emitted close to ground-level, causing elevated pollutant concentrations near busy roads when compared with urban background concentrations [1]. Numerous studies have shown that green-barriers can mitigate PM exposure via reducing the source of PM by covering the surface, absorbing atmospheric PM, and influencing meteorological factors [2].
The following work is part of the "TESTI" project for the restoration of a green belt in Viale Fulvio Testi (Milan) with the aim to evaluate the effectiveness of vegetation on atmospheric pollutants. A preliminary study was carried out within this work to determine the concentrations of pollutants currently present on the site. During the sampling an Optical Particle Counter (Grimm) allowed to determine PM_{10}, $PM_{2.5}$ and PM_1. Ethalometer, SOOTSCAN and TCA (Magee Scientific) were used to determination black carbon and total carbon. For the sampling of the gas phase, two NO_X (Environnement S.A) and O_3 (Environnement S.A) analyzers were employed. Concentrations of atmospheric particulate matter PM_{10} and $PM_{2.5}$ (by gravimetric method) were determined with a resolution time of 24h (FAI Hydra Dual Sampler). Ionic composition of PM_{10} (Fig. 1) reflects the trend of the winter season, characterized by a prevalence of nitrates on sulphates [3]

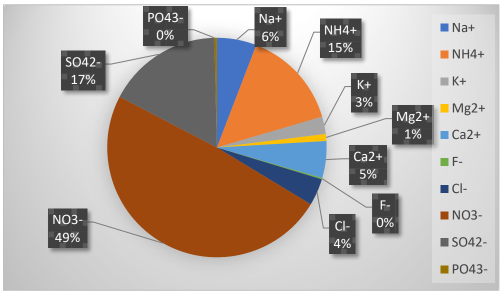


Fig. 1 - Average ionic composition of PM_{10}

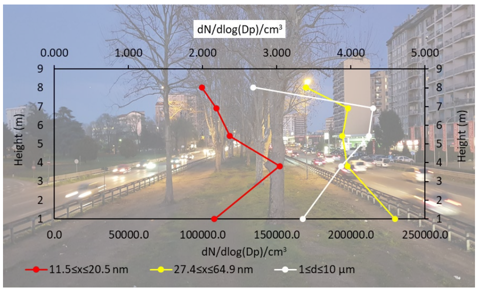


Fig. 2 - Dimensional distribution of the particles along the vertical profile (08:00 – 10:00 a.m.)

Through a NanoScan SMPS (TSI) and an OPC (Grimm) the vertical and horizontal profiles of the atmospheric particulate were realized at the sampling site (11.5 nm-10 µm). In the morning and in the evening the particles concentrations are high and decrease with increasing distance from the guard rail (up to 4-5 meters). The particles remain stable in concentrations up to about 5 meters along the vertical gradient (Fig. 2), so the particles fluctuate and gradually decrease. The trend of concentrations is typical of a high vehicle traffic site. This study represents the starting point to verify the ability of vegetation in retaining the atmospheric particulate matter in Viale Fulvio Testi site and would be applicable in other urban contexts.

[1] Goel et al., (2016), *Environmental Pollution* 214, 54-69.
[2] K.V. Abhijith et al., (2017), *Atmospheric Environment* 162, 71-86.
[3] Perrone et al., (2012) *Science of the Total Environment* 414, 343-355.

Aknowledgements: Metropolitan City of Milan is financing and developing, in cooperation with the Regional Agency for Agricultural and Forestry Services (ERSAF) and Lombardy Foundation for the Environment the ''TESTI'' project that aims at renewing and improving safety of Viale Fulvio Testi (Milan).

Aerosol characterization from the tropics to the North Pole

N. Losi[a], L. Ferrero[a], A. Bigogno[a], A.M. Cefalì[a], L. Scibetta[a] and E. Bolzacchini[a]

[a] Department of Environmental Sciences, University of Milano Bicocca, Milano, 20126, Italy

Aerosols affect the climate both directly (absorption and reflection of sunlight) and indirectly (on cloud coverage and properties, and thus also on the formation of precipitation), triggering complex feedbacks at different spatial and temporal scales. Therefore the aerosol properties are fundamental to describe its role in climate modifications [1] and they are connected to the aerosol chemistry. For this reason we participated in two AREX (Arctic-Expedition, summer 2018 and 2019) scientific cruises from Gdansk to the Arctic and one (EUREC^{4}A, January-February 2020) in the North Atlantic, eastward and south-eastward of Barbados, aiming at the determination of the aerosol chemical composition and properties from the Tropics to the North Pole. The research vessels (r/v Oceania and r/v Atalante) were equipped with a high volume sampler ECHO-PUF (sample flow of 180 l/min) by Tecora to collect TSP on quartz filters and infer the aerosol chemical composition by laboratory analysis: ion chromatography to determine the Water-Soluble Inorganic Ions concentration; SOOTSCAN and TCA (by Magee Scientific) to determine Black Carbon, Total Carbon, water soluble and insoluble Organic Carbon contents. Additionally, nano-particle number concentration and particle from 0.25 up to 32 μm number concentration were measured in real time. Moreover an Aethalometer (AE-33, Magee Scientific, 7-λ) allowed to infer eBC and LAA concentrations and absorption coefficients. Regarding AREX, in figure 1 we can see how the dominant aerosol chemical markers are related to primary marine emissions. The most present ions are chloride and sodium, which can be taken as reference parameters to quantify sea spray inputs (mean concentration of 2.73 μg/m^3). Moreover it was possible to determine the sea salt contribution to the observed concentrations of the ions present also in seawater as major constituents: more than 80% of them originated from sea salt; the sea salt contribution to sulphates is the lowest (it can also be transported from lower latitudes and have a secondary origin). The organic carbon accounted for more than 85% of the total carbon; the remainder is elemental carbon (≃BC), transported or emitted in the Arctic region. BC is a light absorbing aerosol and thus plays a key role in Arctic warming, especially through the energy transport northwards induced by its storage at mid-latitudes; indeed the latitudinal averages of eBC progressively decrease moving northward (European background ≃ 1 μg/m^3 and arctic background ≃ 4-9 ng/m^3). Regarding EUREC^{4}A eBC concentrations ranging from 1 to 2.2*10^3 ng m^{-3} (mean value 549 ± 5 ng m^{-3}); instead Nano-particle total number concentration (N) range from 200 to 4*10^4 #/cm^3 (mean value 4.86*10^3 ± 1.1*10^2 #/cm^3). Evaluating the ratio N/eBC, we have obtained some preliminary information on the formation of secondary aerosol: its relative importance seems to be greater for the first part of the cruise and its trend seems to be in agreement with the size variation of nanoparticles along the cruise (generally where N/eBC is greater, the size is smaller).

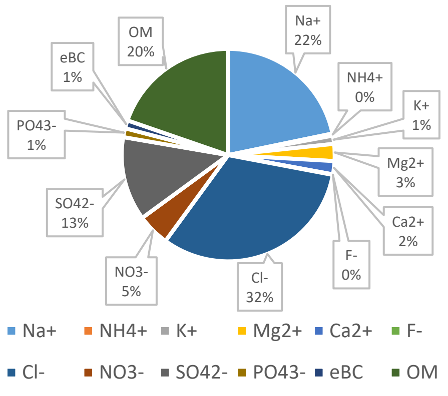


Figure 1. Relative mass percentages (AREX2019)

[1] L. Ferrero, et al., *Atmosphere* **2019,** 10.2, 54.

X-Ray Diffraction of Non-Exhaust Emissions generated from Braking: How to Assess the Phase Composition of the Crystalline Fraction

A. Mancini [a,c], F. Bertasi [a], A. Bonfanti [a], L. Gigli [b], L. Ferrero [c], E. Bolzacchini [c]

[a] Brembo S.p.A., CGF Research & Development, Viale Europa 2, 24040 Stezzano (BG); [b] ELETTRA Sincrotrone Trieste, MCX Beamline, 34149 Basovizza (TS); [c] Università di Milano Bicocca, Dipartimento di Scienze Ambientali e della Terra (DISAT), Piazza dell'Ateneo Nuovo 1, 20126 Milano (MI).

The road transport sector generates respectively the 10% and 11% of the total PM10 and PM2.5 emitted in air in EU. These figures increase up to six times when the urban environment is specifically considered [1]. Particulate matters (PMs) generated by the road transport sector are usually divided in the two following categories: *i)* Exhaust emissions, referring to particulates generated by combustion engines; and *ii)* Non-exhaust emissions, grouping particulates generated by the wear of brakes, tyres, clutches and roads, together with associated resuspension effects. Nowadays, non-exhaust emissions are assessed to contribute in similar weight to the exhaust ones within the road transport category [2]. With specific reference to non-exhaust emissions, particles generated as primary emission from braking systems are estimated to contribute to the PM$_{10}$ and PM$_{2.5}$ fractions respectively by 55% and 21% [3].

Brakes emissions are generated by the wear of the mechanical parts involved in the operation, *i.e.* the friction couple composed by braking disc (BD) and the friction material (FM) from the braking pads. The worn material produced by the BD and FM rubbing surfaces has wide dimensional distribution, ranging from nano- and micro-sized particles emitted in air to millimeter-scaled platelets and chips falling to the ground. As far as human health is concerned, the former ones are of main interest due to their capability to penetrate deeply into the lung structures. Conversely, when soil or aquatic environmental assessments are considered, the latter ones represent the main subject.

As far as both toxicological and environmental studies, the investigation of the chemical composition of the brake emissions has gained momentum in the recent years [4-5]. However, only a limited number of observational studies are currently available in the literature, mainly assessing to the elemental composition of particulates generated by brakes, while little information are known on the crystallographic phases comprised in such emissions. Since the knowledge about the chemical compounds composing a substance it is usually more representative and functional than the simple information on its elemental composition, this represents a fundamental field of investigation from a cyto- and eco-toxicological point of view. For these reasons, this contribution proposes X-Ray Diffraction (XRD) analysis as a valuable tool to investigate the phase composition of the crystalline fraction of non-exhaust emissions generated by brakes, both in qualitative and quantitative fashion. More in detail, insights on the variation of Iron-related phases are provided, showing how different friction couples and driving conditions can modulate their distribution. In addition, the detection limit of secondary and minor compounds is also evaluated and discussed.

[1] EEA, "Air Quality Report n°09/2020", *European Environment Agency*, **2020**.
[2] J. Kukutschova, "Non-Exhaust Emissions – Chapter 6: Review of Brake Wear Emissions", *Elsevier*, **2018**, 123-146.
[3] T. Grigoratos, *et al.*, "Brake Wear Particle Emissions: a Review", *Environ. Sci. Pollut. Res.*, **2015**, 22, 2491-2504.
[4] M. Figliuzzi, *et al.*, "Copper-dependent biological effects of particulate matter produced by brake systems on lung alveolar cells, Archives of Toxicology", **2020**, 94, 2965-2979.
[5] A. Mancini, *et al.*, "Novel Approaches for Physico-Chemical characterization of Brake Emissions", EuroBrake2021, **2021** EB2020-EBS-031.

On-gel sampling for analytical investigation of dyes in pictorial artworks: new advances

Adele Bosi [a,b], *Alessandro Ciccola* [a], *Ilaria Serafini* [a], *Valentina Nigro* [c], *Paolo Postorino* [d], *Gabriele Favero* [e], *Roberta Curini* [a]

[a] *Dept. Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185, Rome;* [b] *Dept. Earth Sciences, Sapienza University of Rome, P.le Aldo Moro 5, 00185, Rome;* [c] *ENEA R.C. Frascati, Fusion and Technologies for Nuclear Safety and Security Dept., Via Enrico Fermi 45, 00044, Frascati (RM);* [d] *Dept. Physics, Sapienza University of Rome, P.le Aldo Moro 5, 00185, Rome;* [e] *Dept. Chemistry and Technology of Drugs, Sapienza University of Rome, P.le Aldo Moro 5, 00185, Rome*

The identification of organic materials in pictorial art objects represents a complex issue, especially if compared to the analogue one for inorganic materials, which can be performed through non-invasive and on-site methodologies. If several approaches are available for the sensitive detection of these analytes in the laboratory, the sampling from the art objects represents a delicate phase and it must be performed with reference to the principle on micro-invasivity.

Moving from recent works which exploited the application of silver-loaded gels for the SERS detection of dyes from artworks [1–4], this study explores the potential of an analytical procedure which takes advantage of gel substrates versatility to conduct multi-analytical identification: through Agar-gel substrates [5], organic compounds are directly sampled from pictorial films in order to be analyzed by means of spectroscopic techniques, and successively re-extracted for chromatographic analyses [6].

The methodology was tested on madder lake pigments in three binders: egg yolk, Arabic gum, and beeswax, in order to consider its suitability for pictorial materials recurring in archaeological matrices. Several protocols, including gel preparation and application on mock-ups, were tested to discriminate between mechanical and chemical extraction. For the extraction of the dyes, a novel ammonia-based extraction protocol for efficient preservation of the sensitive but informative glycosyl moieties present in some natural dyes was selected [7]. Optical non-invasiveness of the procedure was measured by means of optical microscopy and colorimetry. The preliminary characterization of the dyes on the gel was performed through multi-spectroscopic approach (UV-Vis-NIR spectroscopy, Surface Enhanced Raman Scattering spectroscopy) and, for a deeper characterization, re-extraction was carried out from gel substrates combined to a clean-up procedure for HPLC-MS analyses. The procedure is going to be tested also on pigments derived from brazilwood and indigo, in complex paint systems and in the presence of inorganic components, where non-invasive analytical techniques produce very limited results.

[1] B. Doherty, B.G. Brunetti, A. Sgamellotti, C. Miliani, *J. Raman Spectrosc.* **2011**, *42*, 1932.
[2] E. Platania, J.R. Lombardi, M. Leona, N. Shibayama, C. Lofrumento, M. Ricci, M. Becucci, E. Castellucci, *J. Raman Spectrosc.* **2014**, *45*, 1133.
[3] E. Platania, C. Lofrumento, E. Lottini, E. Azzaro, M. Ricci, M. Becucci, *Anal. Bioanal. Chem.* **2015**, *407*, 6505.
[4] M. Leona, P. Decuzzi, T.A. Kubic, G. Gates, J.R. Lombardi, *Anal. Chem.* **2011**, *83*, 3990.
[5] M. Bertasa, A. Dodero, M. Alloisio, S. Vicini, C. Riedo, A. Sansonetti, D. Scalarone, M. Castellano, *Eur. Polym. J.* **2020**, *123*, 109442.
[6] G. Germinario, A. Ciccola, I. Serafini, L. Ruggiero, M. Sbroscia, F. Vincenti, C. Fasolato, R. Curini, M. Ioele, P. Postorino, A. Sodo, *Microchemical Journal* **2020,** *155*, 104780.
[7] L. Lombardi, I. Serafini, M. Guiso, F. Sciubba, A. Bianco, *Microchemical Journal* **2016**, *126*, 373-380.

Use of natural gels in the treatment of rusty stains in stone materials of cultural heritage

F. Cardellicchio[a], L. Campanella[b], E. Dell'Aglio[b], R. Reale[b], S.P. Nigro[a], F.Langerame[a], A.M. Salvi[a]

[a]University of Basilicata, Department of Science, Viale dell'Ateneo Lucano 10 - Potenza (PZ) 85100 Italy.
[b]University of Rome 'La Sapienza', Department of Chemistry.

Stone materials of artistic and cultural interest, especially those exposed to outdoor pollution, are often subject to risk of deterioration due to atmospheric agents, first of all particulate matter with its high concentration of acids, carbonaceous particles and microorganisms. Specific chromatic alterations, due to corrosion phenomena, consequently occur to cultural heritages when they are close or containing metal parts, such as kingpins, brackets, nails, decorative elements, stabilization reinforcements etc. [1]. Cleaning is the operation by which elements responsible for these chromatic alterations, important not only from the aesthetic point of view, are removed from the stone. Like any other intervention in the field of cultural heritage, the cleaning phase must be effective, hopefully, but also not damaging the cleaned object and the health of the operator. This double aim is obtained by using safe products and techniques to be chosen among the available ones. A good intervention must be selective, sufficiently controllable and not harmful to the stone material; it has to be selected according to the material constituting the artefact, its state of conservation, and the staining products (composition and structure) to be removed. Iron is chemically very sensitive to the action of chelating agents able to form metal closed structure complexes. Purpose of this work was to evaluate the use of some types of iron chelating agents dispersed in a natural gel consisting of polyvinyl alcohol and sodium alginate for the removal of rust patches from test marbles appositely stained. Attention was paid to the composition of the gel constituents, in order that the final product was effective, easy-to-apply, and not prone to produce alterations and or residues on the treated artefacts. The gelled chelating agents that gave the best results on marble specimens were Deferiprone and Glutathione, two natural products active in vivo at neutral pH, which allowed the effective removal of iron stains on the treated surfaces within a time of 24 hours. Deferiprone is a tridentate chelator widely studied and used in the treatment for iron overload while Glutathione is a tripeptide formed by the three amino acids cysteine, glutamic acid and glycine, which has both chelating and oxidizing properties. Figure 1 shows the adopted procedure and the chromatic variation following just one treatment with Deferiprone. Analytical investigations of XPS photoelectron spectroscopy have been of valid support for the study of the composition of the chromatic alterations and of the material after the treatment operations [2].

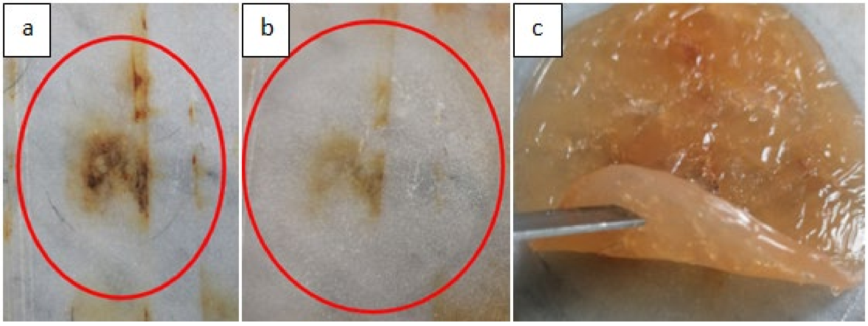


Fig. 1. Carrara Marble treated with Deferiprone. a) before treatment b) after treatment c) gel containing Deferiprone.

[1] R. Reale, PhD thesis, available online, **2017**, 227 pp.
[2] J.E.Castle, H. Chapman-Kpodo, A. Proctor, A.M. Salvi, J Electron Spectrosc. Relat. Phenom. **1999**, 106(1), 65.

Use of natural products for the microorganisms removal from stone church cultural heritage

F.Cardellicchio[a], S.M.Mang[b], L.Scrano[c], F.Langerame[a], S.Berlingieri[a], I. Camele,[b]A.M. Salvi[a]

University of Basilicata, Department of Science (DIS)[a], School of Agricultural, Forestry, Food and Environmental Sciences (SAFE)[b] Viale dell'Ateneo Lucano 10 - Potenza 85100 (PZ), DiCEM [c] Via Lanera, 20 - 75100 Matera, Italy.

Biodeterioration of stone assets is a long term process produced by the microbial communities living and developing on the surface which release organic and inorganic acids, being involved in redox processes of the matrices constituents (bio-corrosion). The understanding of the complex interactions between colonizing organisms themselves, environmental pollutants and chemical degradation processes represent the necessary basis for the diagnostics of monuments degradation status and their specific maintenance. In recent years, the study of natural biocides able to selectively remove biological contamination from stone surfaces has intensified [1,2]. In particular, in this work, the biocidal activity of glycoalkaloids, inserted on proper gelling agents as supporters, was investigated. The use of a Polyvinyl alcohol hydrogel (PVA) based biocompatible gel, suitable to incorporate glycoalkaloids and which can be easily applied to the deteriorated stone artifacts, had been proposed for the bio-cleaning of cultural heritages. The study site was represented by the stone church of San Pietro Barisano (part of the UNESCO heritage) located in Matera (southern Italy) and specifically the hypogeum of the structure, where significant biodiversity was found. The first phase of the work was the investigation of biological communities present on the stone surface favoured by both the microclimate inside the church and the important infiltrations of water. The second phase of the work consisted in the sampling, isolation, identification and characterization of fungal species, present on the deteriorated surface. Preliminary identification, based on a single locus of the ribosomal RNA, (Internal Transcribed Spacer-ITS) reported the presence of few fungal genera such as *Penicillum*, *Botryotrichum, Phialophora* and *Cladosporium*. Further molecular identification and characterization at species level based on multilocus molecular analyses are in progress. Finally, the interesting part of the work concerned the optimization of the biogel composition to be used as a support for the glycoalkaloids extracted from the *Solanum nigrum* plant, in order to evaluate its biocidal activity against the identified microorganisms.
The calcarenite samples characterization was performed by surface analysis using X-rays photoelectron spectroscopy (XPS), before and after the cleaning treatments to verify any alteration due to the gel application. Obtained results will be discussed according to close research literature findings.

[1] L. Scrano, R. Laviano, G. Salzano, M. Santacroce, S.A. De Franchi, J. Baranek, S.A. Bufo, IOP Conf. Series: Materials Science and Engineering, **2020**, 949, 012096.
[2] F. Gabriele, M. Tortora, L. Bruno, C. Casieri, M. Chiarini, R.Germani, N.Spreti, Journal of Cultural Heritage, available online, **2021**.

On the execution techniques of white Attic vases: the case of the Perseus crater in Agrigento

Gabriella Chirco[a], Delia Francesca Chillura Martino[b], Monica De Cesare[a]

[a] Dipartimento di Culture e società, Università degli Studi di Palermo, Viale delle Scienze ed.15, Cap 90128, Palerm; [b] Dipartimento STEBICEF Università degli Studi di Palermo, Viale delle Scienze ed. 17, Cap 90128, Palermo

The white ground crater by the Phiale's painter (450-440 BC) exhibited in the Pietro Griffo archaeological museum in Agrigento [1] depicts scenes from the Perseus myth realized on a white slip. The vase is of utmost importance for archaeologists because the painting technique features figures drawn on a white ground with remarkable daintiness and attention to detail (Figure 1). This kind of vase is a valuable rarity which use is documented in elitist funeral rituals.

Figure 1. The Perseus Crater, side A and B

The painting technique is scarcely documented concerning both compositions of used pigments and binders and realization technique [2,3].

This study aims to investigate the constituent materials and the executive technique. The investigation was performed by exploiting non-destructive and non-invasive procedures in situ. Portable X-ray fluorescence and Fourier-transform total reflection infrared spectroscopy [4] complemented the use of visible and ultraviolet light photography to get an overview and specific information on the vase. The vase resulted in an objective good state of conservation, and the succession of the construction phases with different firing temperatures was evidenced.

[1] M. De Cesare, D. Chillura Martino, E. Caponetti, M.L. Saladino, V. Renda, La pittura vascolare attica a fondo bianco: la prospettiva archeologica, l'apporto dell'indagine scientifica in *Scienza e archeologia: un efficace connubio per la divulgazione della cultura scientifica*, 2017, 59-74. ISBN 978-884675210-9

[2] C. Berthold, K.C. Zimmer, O.Scharf, U. Koch-Brinkmann, K. Bente, Nondestructive, optical and X-ray analytics with high local resolution on attic white-ground lekythoi, *Journal of Archaeological Science: Reports* 2017, 16, 513–520.

[3] I. Meissner, Weissgrundige Lekythen, Fallstudie WS2008/2009. Lehrstuhl für Restaurierung, Kunsttechnologie und Konservierungswissenschaft, 2009, TU-München.

[4] G.Chirco, E.C. Portale, E. Caponetti, V. Renda, D. Chillura Martino, Investigation on four centuripe vases (late 3rd-2nd cent. B.C.) by portable X-ray fluorescence and total reflectance-FTIR, *Journal of Cultural Heritage* 2021, 48, 326-355. https://doi.org/10.1016/j.culher.2020.10.011.

Air quality monitoring for preventive conservation in the Santuario della Beata Vergine dei Miracoli di Saronno (VA)

Paola Fermo[a], Valeria Comite[a], Vittoria Guglielmi[a], Roberto Bonomi[b], Carola Ciprandi[b], Carlo Mariani[c], Antonio Faggiano[d], Maria Ricciardi[d], Antonio Proto[d]

[a] Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, Milan, Italy; [b]Scuola di restauro di Botticino, Botticin (BS), Italy; [c] Architetto, Via Giuseppe Giusti n. 21/B, Seregno (MB), Italy; [d]Department of Chemistry and Biology "A. Zambelli", University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA) Italy

The sanctuary of the Beata Vergine dei Miracoli was erected in 1498 on the site of a miracle. The greatest Lombard artists of the time were commissioned to embellish the sanctuary with paintings and sculptures. The most famous painter of that time, Bernardino Luini, decorated the apse and presbytery of the church with some masterpieces such as the Marriage of the Virgin. The dome, on the other hand, was frescoed by Gaudenzio Ferrari, another outstanding Lombard painter of the 16th century. In addition, two marvelous wooden sculptural groups, the Deposition (1528-1529) and the Last Supper (1531-1532) (Fig. 1) were carved by the sculptor Andrea da Corbetta and decorated and gilded by Alberto da Lodi.

Recently it was decided to undertake a study of air quality and microclimatic conditions inside the church. At this purpose both particles and gaseous pollutants were monitored. Aerosol particulate matter (PM) concentrations were evaluated by means of an optical particles counter and at the same PM chemical composition was investigated on samples collected on quartz fiber filters in order to assess the main constituents such as ions and carbonaceous fraction (i.e. OC, organic carbon, and EC, elemental carbon). NO_2, CO_2 and BTX were collected by means of passive cartridges. The measurements, as regards both pollutants concentrations as well as microclimatic conditions (temperature and relative humidity), were carried out in different places and heights inside the church with the objective to assess the impact of air quality and indoor conditions particularly on the precious wooden statues and to acquire information useful for their preventive conservation and to set-up a maintenance program.

Fig .1 Santuario della Beata Vergine dei Miracoli, Saronno (VA): the Last Supper by Andrea da Corbetta and Alberto da Lodi.

A multi-analytical approach to understanding the ageing behaviour of modern paints in graffiti and urban art works

G. Pellis[a], L. D'Amico[a], M. Bertasa[a], C. Ricci[b], A. Scarcella[b], P. Croveri[b], D. Scalarone[a]

[a] Department of Chemistry, University of Turin, Via Pietro Giuria 7, 10125 Turin (Italy); [b] Centro Conservazione e Restauro "La Venaria Reale, Via XX Settembre 18, 10078 Venaria Reale (Italy)

The preservation of modern graffiti and murals against time and environmental effects is one of the emerging challenges of Cultural Heritage. Murals are nowadays increasingly exploited as decorations to requalify places (e.g. Barriera di Milano in Turin) or to recall significant events. However, time and atmospheric agents prevent murals from lasting for decades. Furthermore, the interest in conserving murals still lacks far behind of studies on the mechanisms leading to their degradation due to pollution, UV exposition and atmospheric agents. Usually, paints are chosen by street artists merely on artistic considerations and drawing styles, which do not always take into account durability and degradation issues[1]: every artist employs a wide ensemble of materials, frequently changing the application methods. This approach hampers the possibility of implementing a general procedure for preserving murals or restoring those that are already affected by degradation[2]. Consequently, to develop appropriate conservation and restoration strategies, it is important to exactly know the chemical composition of artworks and the degradation processes they may undergo. From a chemical point of view, the main components of paints are the binding medium, pigments and extenders. Additives may be present in small quantities to improve the performances of the paint[3] as shelf life, application, durability, as well as apt Health and Safety Executive (HSE)[4]. The precise formulation of every single spray paint is often unknown because of proprietary methods and countless components.

In this research, developed in the framework of CAPuS project, we adopted a multi-analytical plan to study the composition of the most used mural paints and their degradation owing to UV exposure, variation of temperature and humidity. The experimental set was made up of five paint brands, including alkyd sprays and styrene-acrylic products, with four colours on four types of support: microscope slides, concrete, brick and cement plaster. They underwent artificial aging in accelerated outdoor condition and several wet-dry cycles. The techniques employed were colorimetric measurements to check colour stability, Fourier Transformed Infrared Spectroscopy and Pyrolysis-Gas Chromatography/Mass Spectrometry for characterizing paints. A multi-analytical approach is demanded to provide specific information on polymers, pigments and additives. Although FTIR analyses allow the detection of fillers, classes of binders and pigments, the exact identification of spray paint composition is only possible through a cross-check from Py-GC/MS analyses. Evolved Gas Analysis-Mass Spectrometry was also employed in order to achieve a deeper and more precise degree of information on the composition of the investigated mural paints. EGA-MS was used to obtain information concerning the operating temperatures for multi-shot Py-GC/MS analysis, allowing a selective study of the paint components. The results show that the composition and structure of both alkyd and styrene-acrylic products are affected by aging processes. In particular, the loss of low molecular weight additives and the occurrence of cross-linking processes contribute to the embrittlement of the paint layers and to those decay phenomena, such as cracking, scaling, flaking and fading, often observed on graffiti and murals.

[1] J. La Nasa, S. Orsini, I. Degano, A. Rava, F. Modugno, and M. P. Colombini, *Microchem. J.*, **2016** *124*, 940-948.

[2] A. Bosi, A.Ciccola, I Serafini, M Guiso, F. Ripanti, P. Postorino, R. Curini, A. Bianco *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, **2020** *225,*117474.

[3] T. Learner, *IRUG2 V&A*, **1995** 7-20

[4] E. Jablonski, T. Learner, J. Hayes, and M. Golden, *Stud. Conserv.*, **2003**, *48,*3-12.

Physicochemical characterization of cellulose triacetate-based motion-picture films and a potential approach to avoid vinegar syndrome

Francesca Porpora[1], *Alessia Maiano*[1], *Giovanna Poggi*[1], *Luigi Dei*[1], *Emiliano Carretti*[1]

[1] *Department of Chemistry "Ugo Schiff" and CSGI, University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino, FI, Italy.*

Motion picture films made by cellulose triacetate (a material widely used as support since the late eighties to the early 20th century) are objects subjected to degradation mainly due to the "vinegar syndrome" [1]. This phenomenon [2, 3] concerns the side chain scission through ester hydrolysis induced by water naturally present in the atmosphere, with the formation of hydroxyl groups and the release of acetic acid. Above a critical concentration, acetic acid induces an autocatalytic process causing the progressive degradation of the film support. A secondary effect induced by the acetic acid formed through vinegar syndrome is the hydrolysis of the glycosidic bonds between the saccharide units constituting the backbone [3]. The macroscopic symptoms of these phenomena, such as the deformation of the support and the detachment of the emulsion layer, can strictly compromise the usability of the films [4].

At the moment there are no chemical procedures available to stop this process. The only way to preserve cellulose triacetate motion-picture films is to slow down the kinetics of the hydrolysis reaction (which has an Arrhenius-like dependence from temperature [5]) by storing the films in boxes at low temperatures (around 0 °C) and maintaining humidity below 40% [4]. Unfortunately, once the film is heated back to room temperature, the autocatalytic reaction restarts at the same rate.

Therefore, in order to define an innovative protocol for the restoration and preservation of cellulose triacetate motion-picture films, a preliminary instrumental diagnostic investigation has been carried out on some naturally degraded cellulose triacetate film samples. To minimize the impact of the analyses, non-invasive or micro-invasive techniques were used. The results show that the acetic acid hydrolyzes cellulose triacetate, causing a drastic reduction in the plasticity of the film that appears much more rigid and fragile than a non-degraded one. Moreover, the detachment and loss of part of the photographic emulsion layer are observed. In both these cases, the quality of the images projected on a white screen is partially compromised.

[1] P. Read, M. P. Meyer, "Restauration of Motion Picture Film", *Butterworth Heinemann*, **2000**.
[2] N. S. Allen, M. Edge et al., *Polymer Degradation and Stability,* **1987**, *19*, 379.
[3] M. McGath, S. Jordan-Mowery et al., *Restaur*, **2015**, *36*, 333.
[4] J. Reilly, "IPI Storage Guide for Acetate Film", *Image Permanence Institute*, **1993**.
[5] P. Z. Adelstein, J. M. Reilly et al., *SMPTE J.*, **1992**, *101*, 336.

Occurrence and characterization of microplastics in the Mugnone creek waters (Florence, Italy)

Eleonora De Beni[a], Gabriele Bicocchi[b], Saul Santini[a], Tania Martellini[a], Chiara Sarti[a], David Chelazzi[a], Alessio Monnanni[b], Alessandra Cincinelli[a], Stefania Venturi[b], Valentina Rimondi[b]

[a] *Department of Chemistry "Ugo Schiff", University of Florence.*
[b] *Department of Earth Sciences, University of Florence.*

Due to the rapid growing of industrialization and urbanization of cities, the levels of plastic currently present in the environment became a major cause of concern, so much so that this material is considered a persistent and ubiquitous pollutant, proposed as a new stratigraphic indicator of Anthropocene[1] for its slow degradation in the environment. The accumulation and ecological effects of anthropogenic litter (i.e., microplastics MPs, that are plastic fragments ≤5 mm in diameter), are well-documented in aquatic ecosystems, but the role of urban streams in their transport is not yet clear.

The Mugnone Creek (MC), an urban stream flowing across the city of Florence (Italy) and discharging into the Arno River, is an important study area for understanding the MPs contamination status in waters. For the survey, several sites along the 17-km long MC were chosen[2], including upstream of the urban area of Florence, several urban-impacts located along a congested road and the mouth of the Mugnone in the proximity of the Arno River (Cascine Park). The stream waters were collected in June and December 2020 to evaluate the seasonal variability of the plastic debris.

Water samples were filtered onto glass microfiber filters, 47 mm diameter, and a digital stereomicroscope and Fourier Transform Infrared Spectroscopy (FT-IR) were used for identification and characterization of MPs. To avoid potential MPs contamination, strict quality control measures were adopted. MPs characterization was based on shape, color and size, and the abundance of MPs was reported as the total number of plastic particles in stream water volume.

Greater concentrations of MPs were recorded during the winter as compared to summer season. Blue fibers were the most prevalent MPs, in agreement with various surveys around the world[3] that have evidenced a prevalence of dark fibers as the most common type of anthropogenic litter.

This work represents a preliminary step for understanding the sources and fate of MPs in an urban river ecosystem and, further, investigating the effects on the macrofauna.

1. Zalasiewicz, J. *et al. Anthropocene* **13**, 4–17 (2016).
2. Bicocchi, G. *et al. EGU General Assembly* (2021).
3. Suaria, G. *et al. Sci. Adv.* **6**, 1–9 (2020).

Detection of micro and nano-plastics in marine sponges by a combined micro-FTIR and py-GC/MS approach

Clarissa Raguso [a], *Greta Biale* [b], *Francesco Saliu* [a], *Jacopo La Nasa* [b], *Ilaria Degano* [b], *Davide Seveso* [c], *Paolo Galli* [c], *Marina Lasagni* [a], *Francesca Modugno* [b]

[a] *Earth and Environmental Science Department, University of Milano Bicocca, Piazza Della Scienza 1, 20123 Milano, Italy*
[b] *Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy*
[c] *MaRHE Center (Marine Research and High Education Center), Magoodhoo Island Faafu Atoll, Maldives*

Plastic pollution has been recently recognized as one of the emerging threats to the world's oceans health, especially due to the possible interaction of micro and nano particles with the marine biota [1]. Sponges are aquatic filter-feeding animals, capable to incorporate microscopic foreign particles, thus may be exploited as bioindicator for microplastic. We submitted therefore demosponges sampled from the Maldivian archipelago to a new analytical protocol (Figure 1) that combines morphological observation, by infrared micro-spectroscopy(μFTIR) and analytical pyrolysis coupled with gas chromatography and mass spectrometry [3].

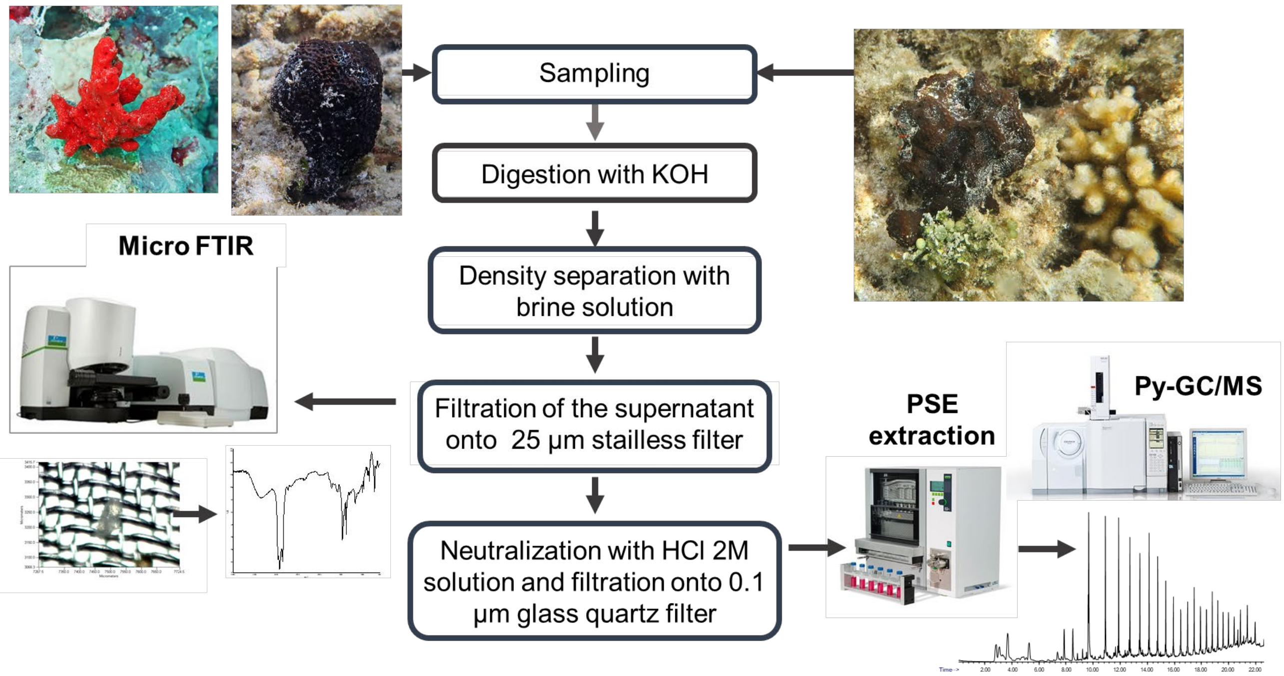


Figure 1. Scheme of the adopted analytical workflow.

[1] A. L Andrady, *Marine Pollution Bulletin* **2011** *62* 1596–

[2] F. Saliu, et al P. *Marine Pollution Bulletin* 2**018,** *136,* 464

[3] J. La Nasa, G. Biale, M. Mattonai, F. Modugno, Journal of Hazardous Materials **2021**, 401, 123287

Extraction of microplastic from marine sediments: a comparison between pressurized solvent extraction and density separation

Nicolo Stile[a], *Anna Sanchez Vidal*[b], *Emir Cetojevic*[c] *Francesco Saliu*[a] , *Marina Lasagni*[a,]

[a] *Earth and Environmental Science Department, University of Milano Bicocca, Piazza Della Scienza 1, 20123 Milano, Italy.*
[b] *Department of Earth and Ocean Dynamics, Faculty of Earth Sciences, University of Barcelona, 08028 Barcelona, Spain*

[C] *BÜCHI Labortechnik AG, Meierseggstr. 40, Postfach, CH-9230 Flawil 1, Switzerland*

Due to the possible adverse effect onto marine organisms, microplastics are considered a threat for the marine environment. Recent reports indicate their presence not only in subsurface water and in coastal sediments, but also in the deep-sea [1]. Notwithstanding, at the present time there are no standardized procedure for microplastic quantification in marine sediments.
In this work, we compared the performance of two different extraction approaches: the common density separation obtained through addition of brine solution and the pressurized solvent extraction (PSE) with organic solvents In order to evaluate microplastic recoveries, we spiked equal aliquots of seafloor sediments with known amounts of polystyrene (PS), polyethylene (PE) and polypropylene (PP) microparticles of different size ranges, and we applied both the extraction procedures. Results showed that the PSE ensured higher recoveries for the smaller size particle fractions (89,2 ± 1.1% in the 50–150 µm range) whereas the density separation enabled precise recoveries for the larger size particles (SD = 1,5%). No significant differences in terms of blanks control were highlighted.

[1] Sanchez-Vidal A, Thompson RC, Canals M, de Haan WP, *PLoS ONE* **2018** 13(11): e0207033.
[2] Stile et al., *Marine Pollution Bulletin*, **2021**, 168112436

Energy policies towards carbon neutrality of the historic centre of Siena

Marchettini N.[a], *Marchi M.*[a], *Meffo Kemda M.*[a], *Niccolucci V.*[a]*, *Pulselli R.M.*[b]

[a] *Ecodynamics Group, Department of Physical, Earth and Environmental Sciences, University of Siena, Pian dei Mantellini 44, Siena, Italy.*

[b] *Laborioso – Laboratory of Research and Innovation for the Sustainability Development Goals, University of Siena, Pian dei Mantellini 44, Siena, Italy.*

The aim of this work is to define the “carbon footprint status” of the medieval historic centre of Siena (Central Italy) by implementing a Greenhouse Gas (GHG) balance in accordance with the 2006 Intergovernmental Panel on Climate Change (IPCC) Guidelines.

The GHG balance results show that Siena occupying a very high position in the carbon footprint scale as it produces a very relevant quantity of carbon dioxide equivalent (53,724 t CO_2-eq) unfortunately not balanced by the sequestration action by local ecosystems (- 324 tCO_2).

Then, specific environmental management policies have been designed with references to the energy efficiency improving (such as energy saving and integrated waste management) and the renewable energies transition. So, it has been appraised their positive impacts on the status of carbon footprint towards decarbonization process.

Among several actions, the installation of photovoltaic (PV) panels of building’s roofs, just outside the medieval walls of Siena City, seems to provide the best performance both in the short and long run. It has been estimated a relevant GHG emissions reduction (-57%) in the short run (10 years) with an installation of about 20 ha of PV panels. In terms of electricity consumption this corresponds to cover both private and public light and electric devices.

Furthermore, the carbon neutral status can be reached in the long run (30 years) with an extra installation of PV panels (+10 ha), covering moreover the public/household electric heating and electric transport.

New strategies for sustainability: the effect of Bio Renewable solvents on polymeric membrane preparation

Francesca Russo[a], *Francesco Galiano*[a], *Alberto Figoli*[a]*

[a] *Institute on Membrane Technology, CNR-ITM, Via P. Bucci Cubo 17/C, Rende (CS) Italy*
*a.figoli@itm.cnr.it

On-goings transition in chemistry and the general effort towards sustainability offer great possibilities for innovation creating great opportunities for new technologies in industrial renewal. The characterizing elements of this chemical transition are the progressive substitution of fossil fuels and the introduction of new alternative platform chemicals such as solvents from renewable carbon sources and/or biomass [1]. This represents a major change in the manufacture system and in their application in the related technologies. Membrane technology is recognized as one of the Best Available Technologies but the preparation of polymeric membrane still required the use of toxic solvents such as N, N-dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP). The replacement of these solvents with new chemicals from biomass valorisation, according the Green Chemistry approach, represent the new goal for producing membranes. The main objective of this work is to study the effect of alternative solvents, in the polyvinylidene fluoride (PVDF) and polyether sulfone (PES) membranes preparation in flat sheet configuration. In particular, the effects of three Bio Renewable solvents such as methyl 5-(dimethylamino)-2-methyl-5-oxopentanoate (Polarclean®) [2,3], dihydrolevoglucosenone (Cyrene^{TM}) [4]and dimethyl isosorbide (DMI) [5] in the polymeric membrane preparation via non-solvent induced phase separation (NIPS) and vapor induced phase separation (VIPS) were studied. These solvents were chosen for their properties such as viscosity, polarity, and boiling point and also for the indispensable prerequisite of dissolving the selected polymer, P at different temperature. The affinity of polymer P- solvent S were studied by Hansen and Hildebrand's solubility parameters (δ) and the phenomenological description of phase inversion was preliminary investigated by phase diagrams, which describe the thermodynamic aspect of P/S/non-solvent NS system. In VIPS-NIPS technique, water was used as a NS in all cases and the different factors that affects the S/NS exchange for producing membranes were also studied. The morphology, pore-size, porosity, hydrophobicity, mechanical properties and performance in term of the water permeability of the produced membranes, were evaluated. All these aspects have been considered for the comparison of the alternative solvents employed in PVDF and PES membranes production.

References

[1] A. Figoli, T. Marino, S. Simone, E. Di Nicolò, X.M. Li, T. He, S. Tornaghi, E. Drioli, Green Chem. **2014**, 16, 4034,4059.
[2] T. Marino, E. Blasi, S. Tornaghi, E. Di, A. Figoli, J. Memb. Sci., **2018**, 549, 192, 204.
[3] F. Russo, R. Castro-Muñoz, F. Galiano, A. Figoli, J. Memb. Sci., **2019**, 585, 166, 174.
[4] T. Marino, F. Galiano, A. Molino, A. Figoli, J. Memb. Sci., **2019**, 580, 224, 234.
[5] F. Russo, F. Galiano, F. Pedace, F. Aricò, A. Figoli, ACS Sustain. Chem. Eng., **2020**, 8, 659, 668.

Environmental characterization of imidazole-based ionic liquids

Mirco Volanti[a], Adam J. Greer[b], Carlos Avendaño[b], Christopher Hardacre[b], Fabrizio Passarini[a,c] and Rosa M. Cuéllar-Franca[b]

[a] *Department of Industrial Chemistry "Toso Montanari", Bologna University, Viale del Risorgimento 4, 40136 Bologna (BO), Italy;* [b] *Department of Chemical Engineering and Analytical Science, The University of Manchester, The Mill, Sackville Street, Manchester M13 9PL, UK;* [c] *Centro Interdipartimentale di Ricerca Industriale – Fonti Rinnovabili, Ambiente, Mare ed Energia e Ambiente, Via Angherà 22, 47900 Rimini (RN), Italy*

The chemical industry has always been at the forefront of continuous research & development of new materials, processes and solutions, as well as being one of the first sectors to question its environmental responsibilities. The combination of these two spheres is at the heart of the definition of sustainable development and today there is no question of innovation unless the environmental aspect is also included. In this sense, decision support tools become fundamental, through which it is possible to guide choices and the development of new solutions towards ever greener versions. Among them, the so-called at early stage (AES) evaluations deserve a noteworthy recognition. They use an analysis approach aimed at studying the environmental performance of processes before its transfer to an industrial scale, with the aim of identifying any critical issues before energy, time and resources are used for their development.[1] In this work, this strategy is used in combination with the principles of green chemistry as a useful tool for the prevention of environmental impact.
Ionic liquids (IL) are certainly one of the main innovations in the recent chemical industry. They have found application in many fields of chemistry thanks to possibility to modulate their properties through changes in composition and chemical structure. From a structural point of view, these compounds are extremely varied and it is estimated that, in principle, they can exist in at least tens of billions of variants.[2] Given the wide range of possible ILs, it is clear that having predictive methods to estimate their properties would be a great advantage. For physical properties this is routinely done, while for environmental characteristics the literature is still lacking.

With this project, we tried to fill this gap by studying the environmental properties of ILs in order to identify possible impact patterns related to their molecular structure. To do this, a family of ILs was identified in which molecules with different structural characteristics could be selected to highlight the environmental contribution of each part of the molecules. The choice fell on the Imidazolium family, which was analyzed by dividing the basic structure of the molecule into different groups (Fig. 1), in according with the synthesis steps of the production pathway. In this way, through the application of the Life Cycle Assessment (LCA) methodology, it is possible to assign to each group of the ILs its own environmental impact. The results, calculated as impacts on the categories of Global Warming Potential, Toxicity and Ecotoxicity, showed a clear trend between impacts and molecular weight of molecules. On the other hand, complex chain configurations do not necessarily lead to higher impacts. The outcomes of this case study are encouraging in the research of impact patterns among ILs (which needs an expansion of the dataset) and showed the potential of LCA applied to predictive models.

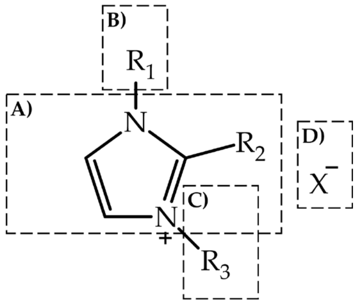


Figure 1 - Generic synthesis steps in the production of Imidazolium ILs

[1] A. C. Hetherington, A. L. Borrion, O. G. Griffiths, M. C. McManus, *Int. J. Life Cycle Assess.* **2014**, *19*, 130–143.
[2] H. Niedermeyer, J. P. Hallett, I. J. Villar-Garcia, P. A. Hunt, T. Welton, *Chem. Soc. Rev.* **2012**, *41*, 7780–7802.

Formation and fingerprints of polychlorinated dioxins and furans in a sintering plants from iron and steel industry

Nicola Cardellicchio[a], Francesco Cardellicchio[b]

[a] *CNR- Water Research Institute, Via Roma 3, 74123 Taranto, Italy*
[b] *University of Basilicata, Department of Science, Viale dell'Ateneo Lucano 10 – 85100 Potenza, Italy*

Due to their toxicities, persistence, and potential to accumulate in the tissues of organisms, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs) are classified as persistent organic pollutants (POPs) from Stockholm Convention. In an integrated industrial plant, like that of Taranto, the production of steel involves a series of processes whereby iron is extracted from ores and converted to steel. One of these is the sintering process, that is a high temperature treatment necessary to obtain a product suitable for blast furnace feedstock.

The sintering processes in integral cycle steel plants are the primary source of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDDs/Fs) whose distribution depends on the composition of the minerals used in the mixture and the conditions of the process (temperature, time, presence of catalysts) [1,2].

This paper discuss about the formation of dioxins/furans from the iron sintering plant of Taranto (Southern Italy) including a discussion on the sintering characteristics, emission control and pollution reduction techniques. The processes by which dioxins/furans are formed are not completely understood.

According to heterogeneous mechanisms, PCDDs/Fs are formed mainly through the two pathways: (a) "*de novo*" synthesis, starting from macro-molecular carbon or polycyclic aromatic hydrocarbons (PAHs) and (b) condensation reactions starting from molecular rearrangement of precursor compounds, such as chlorinated phenols. These assessments are extremely important both for the reduction of atmospheric emissions and for understanding the type of compounds emitted, which are important from a toxicological point of view.

In this paper, various technologies are illustrated for the reduction of emissions, such as injection of coal dust upstream of the electro filters or addition of amines (eg urea) in the agglomeration mixture. The assessment of atmospheric emissions of PCDDs/Fs and the analysis of congeners distribution (fingerprint) indicates a greater presence of chlorinated furans compared to dioxins. Furans made up about 88% of the total emission, dioxins about 12%.

The characteristic profile of congeners in atmospheric emissions was characterized by 1,2,3,7,8 PeCDF and OCDF. The PCDFs/PCDDs ratio > 1 confirmed for these compounds the possibility of a "*de novo*" synthesis on coal particles. The examination of these fingerprints proved to be an effective tool to evaluate the influence of emission sources on environmental contamination, even if diffusion, transport and degradation processes can alter the distribution of congeners in the various matrices.

[1] D.S.Drage, E. Aries, S. Harrad, *Science of the Total Environment*. **2014**, 485, 497.
[2] L. Qian, T. Chun, H. Long, J. Li, Z. Di, Q. Meng, P. Wang, *Process Safety and Environmental Protection*. **2018**, 117, 82.

Green synthesis of glycerol-derived surfactants and carbonates for environmental applications

Prisco Prete[a], Tommaso Tabanelli[b], Federico Bella[c], Antonio Proto[a], Raffaele Cucciniello[a,]*
a Environmental Chemistry Group (ECG), Dep. Chemistry and Biology, University of Salerno, Via Giovanni Paolo II, 132 Fisciano (SA), Italy

b Dep. of Industrial Chemistry "Toso Montanari", University of Bologna, Viale del Risorgimento,4 Bologna, Italy

c Department of Applied Science and Technology – DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

**rcucciniello@unisa.it*

Nowadays, with the continuous increase of the biodiesel demand significant amounts of glycerol are put on the market (2.5 Mt in 2020) and will represent one of the major worldwide drop-in chemicals for the near future. Among the various possibilities for the production of a wide spectrum of molecules (fine chemicals, commodities, fuel additives, specialities) starting from glycerol, the production of epichlorohydrin (ECH), mostly used in the production of epoxy resins, is an important industrial reality.
As a matter of fact, Solvay started in 2011 the glycerol-based production of epichlorohydrin, the so-called Epicerol® process that actually supports the traditional process based on the chlorination of propene at elevated temperatures. Recently, we demonstrated that glycidol can be obtained as value-added product from this process [1]. Moreover, bio-based glycidol can be also obtained though glycerol deoxydehydration to allyl alcohol followed by epoxidation reaction [2-3].
We recently reported the conversion of the as-obtained glycidol to several chemicals of high concern as well as polymers [4], solketal [5], diols [6] and monoalkylglyceryl ethers (MAGEs) [7-9].
Other MAGEs of great interests are represented by surfactants when the aliphatic chain is in the range C8-C24. This class of compounds also respect the 10th principle of Green Chemistry because they are fully biodegradable in the environment and show a very low toxicity. Only few studies deal with long-alkyl ether synthesis, usable as bio-surfactants, from direct etherification of glycerol with fatty alcohols however this approach shows several drawbacks and very poor yields (lower than 15 %) and selectivity.
In this work we report on the synthesis of monoalkylglyceryl ethers by glycidol alcoholysis with long-chain alcohols catalyzed by simple homogeneous metal triflates.

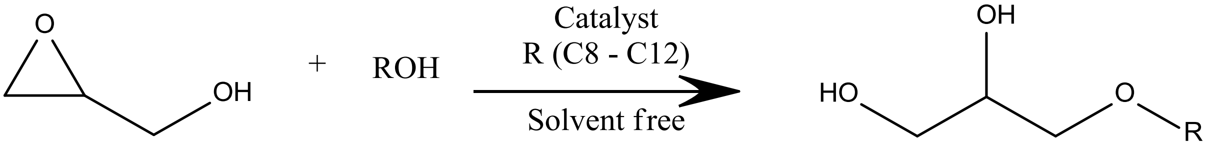


Figure 1. MAGEs synthesis through glycidol alcoholysis.

In the presence of a catalysts based on an Earth-abundant metal, namely Al(OTf)3, the reaction between glycidol and long chain primary alcohols (n-octanol, n-decanol and n-dodecanol) we obtained good conversion to the desired monoalkyl glyceryl ether (MAGE) reaching initial turnover frequency TOF up to 2633 h-1 in the case of octanol.
Furthermore, the preparation of organic carbonates from glycerol is a promising route for high-value added compiunds. Herein, we relied on the preparation of glycerol carbonate and diglyceroltricarbonate evaluating their applicability as electrolyte for Li and post-Li battery [10].

1. D. Cespi, R. Cucciniello, M. Ricciardi, C. Capacchione, I. Vassura, F. Passarini, A. Proto, *Green Chem.* **2016** 18, 4559–4570.

2. M. Lupacchini, A. Mascitti, V. Canale, L. Tonucci, E. Colacino, M. Passacantando, A. Marrone, N. D'Alessandro, *Catal. Sci. Technol.* **2019** 9, 3036–3046.
3. M. Ricciardi, F. Passarini, C. Capacchione, A. Proto, J. Barrault, R. Cucciniello, D. Cespi, *ChemSusChem* **2018** 11, 1829–1837.
4. G. Piana, M. Ricciardi, F. Bella, R. Cucciniello, A. Proto, C. Gerbaldi, *Chem. Eng. J.* **2020** 382, 122934.
5. M. Ricciardi, L. Falivene, T. Tabanelli, A. Proto, R. Cucciniello, F. Cavani, *Catalysts* **2018** 8, 391.
6. R. Cucciniello, C. Pironti, C. Capacchione, A. Proto, M. Di Serio, *Catal. Commun.* **2016** 77, 98–102.
7. R. Cucciniello, M. Ricciardi, R. Vitiello, M. Di Serio, A. Proto, C. Capacchione, *ChemSusChem* **2016** 9, 3272–3275.
8. M. Ricciardi, F. Passarini, I. Vassura, A. Proto, C. Capacchione, R. Cucciniello, D. Cespi, *ChemSusChem* **2017** 10, 2291–2300.
9. F. Della Monica, M. Ricciardi, A. Proto, R. Cucciniello, C. Capacchione, *ChemSusChem* **2019** 12, 3448-3452.
10. G. Rokicki, P. Rakoczy, P. Parzuchowski, M. Sobiecki, *Green Chem.* **2005** 7, 529-539.

Removal of atrazine from water using electrochemical process

Pasquale Iovino[a,b], *Angelo Fenti*[c], *Giovanni Falco*[a]

[a]*Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, University of Campania "Luigi Vanvitelli", via Vivaldi 43, Caserta, Italy;* [b]*Environmental Technologies, University Spin-Off of University of Campania "Luigi Vanvitelli", Via Vivaldi, 43, Caserta, Italy;* [c]*Department of Engineering, University of Campania "Luigi Vanvitelli", 81031 Aversa (CE), Italy.*

Atrazine (ATZ) is an herbicide used since 1958 in large quantities to destroy weeds in wheat and cornfields. It is the most common herbicide in the United States, after glyphosate[1]. The ATZ function is to block the photosynthesis process of the plant, averting the reduction of CO_2 into carbohydrates. Atrazine is moderately soluble in water. Once it enters the water compartments, its half-life increases to several years. In Italy, the use of atrazine was banned in 1992 but its presence in groundwater exceeds the maximum permitted concentration limit (0.1 µg / L). Considering its toxic effects on aquatics species and human health, many studies aim to develop efficient treatment technologies for the removal of ATZ from water. Among them, the electro-oxidation (EO), technique belonging to the class of advanced oxidation processes (AOPs) has been successfully applied to degrade and mineralize ATZ in water sources[2]. The goal of the present work is to determine the effectiveness of the removal of atrazine by electro-oxidation using platinum electrodes. The impact of several process parameters such as current intensity, ionic strength, and the presence of different electrolytes (NaCl, $NaClO_4$, $NaNO_3$), on the removal of ATZ, has been evaluated. Moreover, the effect of the concurrent presence of another pollutant in solution such as Trimethoprim (TMP) on the ATZ degradation has also been investigated. The addition of NaCl in the EO of organic compounds can lead to the formation of chlorine (Cl_2), hypochlorous acid (HClO), hypochlorite (ClO^-) ion that can oxidize organic compounds. The results of this work show that the EO treatment of ATZ using platinum electrodes improves both with increasing current intensity and NaCl concentration. The presence of $NaClO_4$ or $NaNO_3$ salt in solution does not lead to the generation of further oxidizing species and the degradation of atrazine occurs in a longer time than that seen with NaCl (Figure 1.a). The results of the degradation treatment of ATZ, with the concurrent presence of TMP, show that the latter organic compound is more easily oxidizable than ATZ (Figure 1.b).

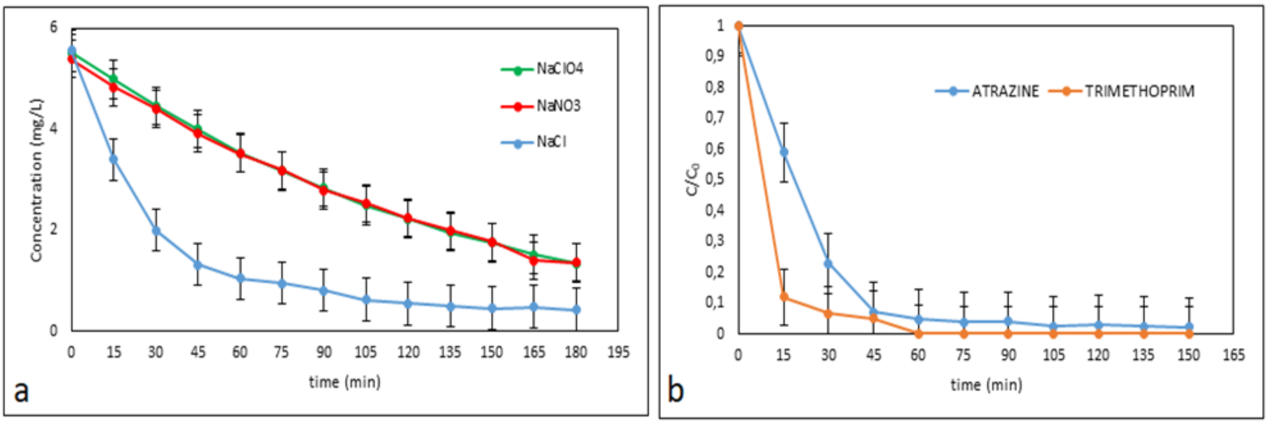


Figure 1.a: ATZ electroremoval run in the presence of NaCl 80 mM or $NaClO_4$ 80 mM or $NaNO_3$ 80 mM, with current intensity I=0.10 A; **Figure 1.b**: ATZ and TMP electroremoval run in the presence of NaCl 80 mM, with current intensity: I=0.20 A

[1] D. A. Belluck, S. L. Benjamin, T. Dawson, Groundwater Contamination by Atrazine and Its Metabolites, Risk Assessment, Policy, and Legal Implications.
[2] Simon Komtchou, et al., Removal of atrazine and its by-products from water using electrochemical advanced oxidation processes, Water Research 125 (2017) 91-103.

Characterization of the chemical contamination of the organic fraction obtained from separate waste collection within the waste recovery value chain

Luca Rivoira[1], Michele Castiglioni[1], Irene Ingrando[1], Vander Tumiatti[2], Francesco Lenzi[2], Maria Concetta Bruzzoniti[1]*

[1]Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria 7, 10125, Torino, Italy
[2]Sea Marconi Technolgies, via Ungheria 20, 10090, Collegno, Italy
luca.rivoira@unito.it

Nowadays, international and national waste directives prioritize not only the recycling of wastes, but also material and energy recovery from wastes themselves. Among the several waste categories, organic wastes (including its fraction deriving from solid urban wastes-FORSU) can be converted into new resources, re-entering into the production cycle through the anaerobic digestion and the composting practices. Such processes promote the recovery both in terms of energy and material, producing biomethane and compost respectively, thus closing the circle of circular economy.
However, one aspect that must be considered is the quality of the recovered products so obtained, which is strongly dependent from the quality of the waste feedstock. Indeed, the assessment of contamination by organic and inorganic micropollutants possibly present in FORSU is of mandatory importance to produce a high-quality compost, which is frequently used as a soil improver and that is demonstrated to contribute, together with the application of sustainable agricultural practices, to reduce desertification and soil erosion.

Differently from compost, methods to evaluate the contamination from organic micropollutants in FORSU are rarely investigated. Based on the above-mentioned assumptions, the aim of the presented work was to innovatively develop an analytical method for the extraction and quantification of selected organic and inorganic micropollutants in FORSU samples. In detail, this study focused on the determination of 16 polycyclic aromatic hydrocarbons (PAHs), and 14 polychlorinated biphenyls (PCBs, including dioxin-like compounds), as well as toxic metals (Sn, Cd, As, Cr, Ni, Pb, Sb, Se).
To what concern organic micropollutants, a microwave assisted extraction (MAE) technique was successfully optimized to extract PAHs and PCBs, through the study the effects of extraction temperature and solvents. Purification of the extracts was obtained by means of a silica-based solid-phase extraction cartridge, to promote the elimination of co-extracted interfering polar compounds, followed by a sulfuric acid treatment, to oxidize organic interfering species still present. The analysis was carried out by means of gas chromatography coupled with mass spectrometry (GC-MS). Extraction yields of the optimized method, calculated after fortification of FORSU samples with isotopically marked surrogates, were quantitative for all the analytes, with RSD% below 8.6%, despite the complexity of the matrix.
For metal analysis, the sample was mineralized by microwave-assisted procedure with HNO_3 and H_2O_2, and the analysis were performed by inductively coupled plasma mass spectrometry, ICP-MS.
Finally, both the methods were applied to the quantification of target analytes in FORSU samples belonging from a local treatment plant (Piedmont, Italy), comparing detected concentration with the only national legislative requirement, i.e. DGRV 235/09 normative.

Acknowledgements

The authors acknowledge Finpiemonte and Regione Piemonte for funding (BIOENPRO4TO- 333-201)

“New LIFE for Mar Piccolo”: Optimization of the purification pilot plant

A. Di Leo, N. Cardellicchio, M. Calò, L. Spada, S. Giandomenico

CNR- Water Research Institute, via Roma 3,74123, Taranto, Italy

The main object of A New LIFE for Mar Piccolo project is the requalification of the Mar Piccolo basin (Ionian Sea, Southern Italy thought to restore a reasonable portion of the basin (about 3000 square meters) using a purification pilot plant based on membrane microfiltration able to protect the present ecosystem.

This approach will allow us to bring down contamination of PCBs, PAHs and heavy metals that are the principal contaminants present in the sediment [1, 2] and consequently in the water column, reaching concentrations within the limits imposed by existing National and Community legislation.

These pollutants, besides, representing a serious disturbance to the delicate balance of the basin, have also affected mariculture activities, with significant damage to this economic sector of national importance.

In order to have an eco-friendly plant, a photovoltaic system able to produce the energy needed to ensure the plant self-sufficiency will be installed.

Moreover, the project aims to provide valuable tools for the sustainable management of marine areas to bodies in charge.

For this purpose, an intervention protocol for the environmental recovery of Italian and European coastal marine sites (inland lagoons, port areas, etc..) with similar pollution problems to those of the Mar Piccolo of Taranto will be developed.

The development of this protocol will include the construction of a multi-assay diagnostic kit for assessing the quality of marine waters.

At the end of the project activities, the reclaimed area of 3000 square meters will have its sea bottom free of bioavailable pollutants and it will be again usable.

Therefore, the prototype developed during the project can be re-used, and in case re-modulated, for reclaiming wider areas within Mar Piccolo and in other Italian and European marine and coastal areas.

In this work we show optimization, operation and verification of the purification pilot plant. This optimization process made it possible to obtain a microfiltration feed with a constant composition, with a concentration of sediment particles in the water entering the microfiltration system of approximately 0.24 g/L. This value made it possible to concentrate the feed up to the desired value.

This value made it possible to concentrate the feed up to the desired value and switch to stable operation of the plant within the sheet piling area.

[1] N. Cardellicchio, A. Buccolieri, S. Giandomenico, L. Lopez, F. Pizzulli, L. Spada, *Mar. Poll. Bull.*, **2007**, 55, 451.

[2] N. Cardellicchio, C. Annicchiarico, A. Di Leo, S. Giandomenico, L. Spada, *Environ. Sci. Pollut. Res.*, **2016,** 23, 12495.

Separation and recycling of critical metals from municipal and industrial waste

Torta Gianluca, Fabrizio Passarini, Luca Ciacci, Ivano Vassura

Department of Industrial Chemistry "Toso Montanari", University of Bologna - Alma Mater Studiorum, Viale Risorgimento 4, 40136 - Bologna, Italy.

Metals, in particular the platinum group metals (PGMs) and rare earth elements (REEs), are fundamental for modern technology as they provide essential properties to products such as permanent magnets, rechargeable batteries, catalysts, catalytic converters, superconductors, and similar. With these applications being expected to reduce energy consumption and mitigate the climate emergency, by extension REEs and PGMs can be relevant means for a transition to a greener society. However, the global demand for these strategical raw materials has increased dramatically in recent years. In Europe, a lack of natural deposits and negligible mine extraction make the EU Member States entirely dependent from imports to satisfy the domestic demand. Consequently, it has become an urgent priority to improve and enhance secondary resource supply (i.e., end-of-life products recovery and recycling) as a sustainable way of securing access to these elements. Recycling of metals from urban and industrial waste will make Europe less dependent from import as well as reduce waste disposal and environmental impacts, as recovery and recycling are generally less impacting than primary production.

However, one of the biggest issues with metal recycling is the relative low concentration of these elements in waste streams so that technological and economic issues are often the ultimate limit to a full industrial scale up. As a consequence, most of those critical metals for the European economy[1] are little recycled, if not entirely lost at end-of-life. In this view, this study aims at developing a recycling process for a set of strategic metals from urban and industrial waste. A preliminary selection of metals with significant recycling potentials includes lithium, nickel, cobalt from spent Li-ion batteries[2], neodymium, praseodymium, and dysprosium from permanent magnets[3], indium from liquid crystal displays[4], cerium, lanthanum, palladium, platinum, ruthenium, and gold from waste electrical and electronic equipment[5], and catalysts[6]. Starting from an extensive review of the most recent literature in this field, this work will evolve to focus on the setting of a strategy for the characterization of waste or by-products containing targeted metals. To this aim, innovative and emerging green recycling methods will be investigated, including metal leaching by means of ionic liquids and/or supercritical fluids for the identification, separation and purification of the elements or compounds of interest.

[1]"European Commission, Study on the EU's list of Critical Raw Materials (2020), Factsheets on Critical Raw Materials"
[2] Hans Eric Melin, *Circular Energy Storage*, **2019**, 1-57.
[3] Yang, Y., Walton, A., Sheridan, R. *et al., J. Sustain. Metall., 2016,* **3,** 122–149.
[4] Ata Akcil, Ismail Agcasulu, Basudev Swain, *Resources, Conservation & Recycling*, **2019**, 149, 622–637.
[5] Christian Hagelüken**,** *Platinum Metals Rev*., **2012**, 56, (1), 29–35.
[6] Christian Hagelüken, *Metall*, **2007**, 61, 24-39.

New biodegradable catalysts for photo-Fenton like process for wastewater treatment and reuse in a circular economy perspective

Prisco Prete [a*], *Antonino Fiorentino* [a], *Luigi Rizzo* [b], *Raffaele Cucciniello* [a], *Antonio Proto* [a]

[a] *Environmental Chemistry Group (ECG), Dep. Chemistry and Biology, University of Salerno, Via Giovanni Paolo II, 132 Fisciano (SA), Italy*

[b] *Dep. Civil Engineering, University of Salerno, Via Giovanni Paolo II, 132 – 84084 Fisciano (SA), Italy*

**pprete@unisa.it*

Among all the most effective advanced oxidation processes (AOPs) for urban wastewater treatment Fenton and photo-Fenton process in the presence of $FeSO_4/H_2O_2$ is one of the most investigated. These processes have not been implemented at full-scale due to the requirement of strongly acidic pH (generally $pH < 3$) in order to prevent iron precipitation as hydroxide [1-2]. To overcome this limitation, some alternative processes have been proposed in the last years, including electro-Fenton, heterogeneous-Fenton and Fenton like, which involves either iron chelates or other transition metal - based complexes as soluble catalysts for the activation of H_2O_2 [3-5]

Thus, the development of new suitable ligands from renewable resources able to promote the Fenton like and photo-Fenton like processes for wastewater treatment have been presented in literature to meet the Green Chemistry principles for the preparation of new bio-degradable environmental catalysts through a benign-by-design approach. [6]

In this work, we report on the preparation, characterization and application of iminodisuccinate (IDS) metal complexes (M-IDS).

M-IDS catalysts have been tested as suitable catalysts in Fenton like and photo-Fenton like processes at neutral pH for the degradation of a model compound (phenol, 50 mg/L initial concentration) in water.

Encouraging results have been obtained with photo-Fenton like processes, achieving complete mineralization of phenol (95%) after 60 minutes of treatment.

The applicability of these metal complexes has been also extended to industrial wastewater treatment (olive oil mill wastewater) with excellent results in terms of COD removal.

[1] A. Fiorentino, R. Cucciniello, A. Di Cesare, P. Prete, L. Rizzo, G. Corno, A. Proto, *Wat. Res.* **2018**, *146,* 206
[2] P. Prete, A. Fiorentino, L. Rizzo, A. Proto, R. Cucciniello, *Curr. Opin. Green Sustain. Chem.,* **2021**, *28*, 100451
[3] J. Meijide, P. S. M. Dunlop, M. Pazos, M. A. Sanromàn, *Catalysts*, **2021**, *11*, 85
[4] A. Di Cesare, M. De Carluccio, E. M. Eckert, D. Fontaneto, A. Fiorentino, G. Corno, P. Prete, A. Proto, L. Rizzo, *Wat. Res.* **2020**, *184*, 116194
[5] A. Fiorentino, P. Prete, L. Rizzo, R. Cucciniello, A. Proto, *Submitted* **2021**
[6] T.J. Collins, *Acc. Chem. Res*. **2002**, *35*, 782

Applications of isotope analysis in environmental studies

Massimo Marchesi[a,b*], *Carolyn Montellato*[a], *Luca Alberti*[b], *Ramon Aravena*[c]

and Orfan Shouakar-Stash[a,c]

[a] *Isotope Tracer Technologies Labs, Milano (Italy), Waterloo (Canada);* [b] *Dipartimento di Ingegneria Civile e Ambientale, Politecnico di Milano, Milano (Italy);* [c]*Earth and Environmental Sciences Department, University of Waterloo, Waterloo (Canada)*

[*]*Corresponding author:* massimo.marchesi@it2europe.com

Groundwater and soil quality studies focus on understanding where contaminants come from and the transformations that they may experience in the subsurface geochemical environments.

Environmental isotopes, including Compound-Specific Isotope Analysis (CSIA), are one of the fastest growing tools applied in contaminant studies. Isotopes have been successfully used in determining the contamination source, understanding the fate of contaminants in groundwater, and evaluating the effectiveness of remediation actions including the performance assessment of a broad range of biological (natural and enhanced), chemical, and physical remediation strategies. This contribution will cover a number of case studies with the aim of presenting the latest advancement in isotope analysis, particularly the applications of Compound-Specific Isotopes Analysis (CSIA), for environmantal applications.

The presentation will include a short overview about theory and background, followed by a short presentation of several field case studies. The contribution will cover the application of environmental isotopes, ^{13}C, ^{2}H, ^{18}O, ^{15}N, ^{34}S, $^{87}Sr/^{86}Sr$, ^{37}Cl, ^{81}Br, and Tritium (^{3}H), to trace the origin of contaminants and the attenuation processes that take place in soils and aquifers. The topics comprise groundwater pollution from agricultural sources (nitrate), industrial activities (e.g. LNAPLs, DNAPLs), as well as urban activities. Furthermore, the presentation is designed to present both the latest advancement in ^{13}C-CSIA, ^{37}Cl-CSIA, and ^{2}H-CSIA and the potential applications of CSIA, in an effort to better understand contaminated sites.

Long-chain alkanes as markers of tobacco smoke impact on the environment

Angelo Cecinato [a, b], Catia Balducci [b], Marina Cerasa [b], Mattia Perilli [b], Paola Romagnoli [b], Alessandro Bacaloni [a]

[a] *Sapienza Università di Roma, Dipartimento di Chimica; angelo.cecinato@uniroma1.it*
[b] *Consiglio Nazionale delle Ricerche, Istituto Inquinamento Atmosferico*

The impact of tobacco smoking on the environment is still far from be understood, despite the smoke exhausts have been extensively investigated and hundreds of chemicals have been identified both in its vapors and particulates. Indeed, a number of substances (including nicotine and its family, alkanes, PAHs, and mono-aromatic hydrocarbons) have been in turn proposed as markers of tobacco smoke (TS), and characterized in artificial chambers as well as in interiors directly or indirectly subjected to smokers' action. Nevertheless, the approach has overall addressed to identify new substances or follow the patterns of these toxicants, e.g. the percentages of nicotine released in vapor phase or really inhaled. Apart from these "hot spots of tobacco", no attempt has been made to assess the whole impact of smoking on the environment. Indeed, most TS components are volatile or semi-volatile and are not persistent in the atmosphere. The only exception until now is the use of nicotelline, a minor component of tobacco exhaust, to assess the contribution of TS to PM_{10} in the air [1].

Thanks to chemical characterization of organic fraction of a number of suspended particulates collected in interiors variously exposed to tobacco smoke (namely a frequent smoker home, no smoker homes, hospitals, and universities) as well at open air, we could draw a "tobacco smoke impact index" (TSI%), suitable to estimate the percentage of tobacco smoke in suspended particulate and deposition dust. For this purpose, we used the composition pattern of long-chain n-alkanes ($nC_{28} \div nC_{34}$) and the respective *iso*- and *anteiso*- congeners. In fact, TS exhausts show typical high percentages of *iso*- odd-C and *anteiso*- even-C homologues. Our preliminary results were analyzed in the light of scientific literature, which confirmed the suitability of our approach [2, 3].

TSI% seemed to fit fine in the case of low percentages of TS in aerosols and dusts (e.g., in no smoker homes and public premises), but unfit in locations lived by frequent smokers, where classical markers like nicotine probably provide better results.

[1] N.J. Aquilina, C.M. Havel, P. Cheung, R.M. Harrison, K.F. Ho, N.L. Benowitz, P. Jacob III, *Environ. Int.*, **2021**, *150*, 106417.
[2] D.J. Eatough, L.D. Hansen, E.A. Lewis, *Environ. Technol.*, **1990**, *11*, 1071-1085.
[3] I.G. Kavouras, N. Stratigakis, E.G. Stephanou, *Environ. Sci. Technol.*, **1998**, *32*, 1369-1377.

Chemical extraction on quartz filters for developing a protocol for the determination of elemental and organic carbon using multiwavelength analysis DRI_2015

Lorenzo Scibetta[1], Asta Gregorič[2], Gašper Lavrič[2], Ana Kroflič[3], Martin Rigler[2], Luca Ferrero[1], Ezio Bolzacchini[1]
[1]GEMMA and POLARIS Centre, University of Milano-Bicocca, 20126 Milano, Italy
[2]Aerosol d.o.o., Kamniška 39 A, Ljubljana 1000, Slovenia
[3]National Institute of chemistry, Department of Analytical Chemistry, 1000 Ljubljana, Slovenia
Keywords: Elemental carbon, DRI_2015, chemical extractions, AAE
Presenting author email: l.scibetta@campus.unimib.it

Carbonaceous aerosols frequently account for a large and often dominant portion of fine particulate matter (PM2.5). Their presence in the atmosphere has a significant influence on global warming and severe implications on human health. The fraction of carbon that can be found in PM2.5 is called total carbon (TC), which is commonly categorized into subcategories of elemental carbon (EC) and organic carbon (OC). The thermo-optical analysis method is usually used for OC and EC determination, in which carbonaceous aerosol deposited on the quartz filter is thermally desorbed according to a prescribed temperature protocol, initially in an inert atmosphere (helium) and then in an oxidizing atmosphere (Helium Oxigen). Thermally unstable organic compounds charred during the inert mode to form more stable pyrolytic carbon (PC), which, if not properly accounted for, would be incorrectly reported as EC. Because PC absorbs light, transmission and reflection signals are measured during analysis. The time when the signal value meets the pre-pyrolysis value is called the OC-EC split point [1]. Uncertainty of such OC-EC measurement is mainly triggered by the incorrect determination of the OC-EC split point, which depends on the aerosol OC content, interference from other aerosol components (brown carbon (BrC), metal oxides, inorganic salts, etc) and thermal protocol used for analysis. The DRI Model 2015 Series 2 with 7 wavelengths (405, 445, 532, 635, 780, 808, 980 nm), programmed with EUSAAR_2 thermal protocol for quantifying OC and EC ambient samples (collected with a 500 L/min active sampler in two different areas of Ljubljana and during two different periods) was used in the study. To minimize the charring effect and find a a properly approach to determine a unique OC-EC split point, an analytical pre-treatment of filter samples was studied. These latter were treated with water and different solvents to extract OC fractions. Results show that water is not capable enough for extracting a significant amount of OC (from 15 to 45% of OC extracted). On the opposite, methanol and acetone, or a combination of them with water is sufficient to eliminate the vast majority of OC and BrC from a filter sample (till 77% of OC extracted), resulting in a negligible PC as a result of the analysis. Due to the multi-wavelength nature of the DRI analysis, the Absorption Angstrom Exponent (AAE) was calculated and considered as a promising parameter in determining the correct split point. Figure 2 shows a possible correlation between the initial AAE_0 and its maximum AAE_{max}(He) in the He mode in all the treated samples. When the vast majority of BrC and OC were removed with methanol or with a combination of more solvents, the AAE reached the lowest value. Extractions also affected the position of the OC-EC split point during the analysis. Results display large discrepancies in the split points $t_{s.p.}$ between the 7 wavelengths for the original samples (922 ± 41 s). However, the OC-EC split point resulting in the analysis of well-treated samples agrees well, suggesting the proposed treatment as a favoured way to minimize and maybe eliminate the PC influence of the EC data.

References[1] Cavalli, F., Viana, M., Yttri, K. E., and Genberg, J.: Toward a standardized thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, 79–89, 2010.

Determination of fragrances in interiors

Martina Garofalo [a b], *Angelo Cecinato* [a b], *Catia Balducci* [b], *Marina Cerasa* [b], *Alessandro Bacaloni* [a]

[a] *Sapienza Università di Roma, Dipartimento di Chimica; angelo.cecinato@uniroma1.it*
[b] *Consiglio Nazionale delle Ricerche, Istituto Inquinamento Atmosferico*

Fragrances and essences (F&Es) have nowadays ascertained as contaminants of interiors, due to the wide presence of these chemicals in personal care and house product formulas [1, 2]. Indeed, their occurrence has been demonstrated in the air of homes and cars as well as of public premises like schools, universities and hospitals. Despite their worldwide use, fragrances belong to the class of emerging organic contaminants, also known as endocrine disruptors. In fact, though F&Es do not seem to display carcinogenic properties, however they can give raise to long- and short-term health problems, e.g. inflammation of skin, eyes and throat, allergies, and even heart, metabolism and brain difficulties as well as gene damaging [3, 4]. Most F&Es are semi-volatile and exist overall as vapours, nonetheless they have been observed also in airborne particulates (PM_{10}, $PM_{2.5}$) and in deposition dusts of interiors; that worsens the exposure of humans to these chemicals, because it is not restricted to inhalation but depends also on ingestion and contact paths. On the other hand, that makes necessary to collect both gas and particle fractions to draw information about the impact of F&E in indoor environment; that can be achieved by using filter-cartridge trains able to retain quantitatively the targeted compounds. As for analytical procedures, usually they consist of solvent extraction/thermos-desorption coupled with GC-MS detection.

A dedicated procedure was optimized to determine the concentrations of F&Es in the interiors. Airborne particles ($PM_{2.5}$) were collected on PTFE membranes, while the gas fraction was retained on XAD-2 cartridges. The analytes were recovered from XAD-2 through elution with acetone, and from filters through extraction in ultrasonic bath; after solvent reduction, F&Es were determined through GC-MSD operated in SIM mode. The recovery efficiency, LoD and LoQ values were evaluated. The procedure was applied to a set of samples collected in two locations, which confirmed the occurrence of F&Es in the interiors as well as outdoors.

[1] J. P. Lamas, L. Sanchez-Prado, C. Garcia-Jares, M. Llompart, *J. Chromatog. A*, **2010**, *1217*, 1882–1890.
[2] M. Fontal, B. L. van Drooge, J. O. Grimalt, *J. Chromatog. A*, **2016**, *1447*, 135–140
[3] E. Uhde, N. Schulz, Atmos. Environ., **2015**, 106, 492-502
[4] P. Wolkoff, G. D. Nielsen, *Environ. Int.,* **2017**, *101*, 96–107.

Emerging organic contaminants in dusts of hospital premises

Angelo Cecinato [a, b], *Catia Balducci* [b], *Mattia Perilli* [b], *Paola Romagnoli* [b], *Alessandro Bacaloni* [a]

[a] *Sapienza Università di Roma, Dipartimento di Chimica; angelo.cecinato@uniroma1.it*
[b] *Consiglio Nazionale delle Ricerche, Istituto Inquinamento Atmosferico*

Hospital interiors are affected by a number of toxicants, some of which are peculiar owing to people hosted (patients and daily service frequenters), to activities carried out and chemicals used there (e.g., radiotherapy and disease screening; pharmaceuticals, cleaning products and disinfectants). Hence, hospital workers and visitors suffer exposure to unknown amounts of toxicants, whose impact on health is far from being assessed. Apart organic contaminants that are common outdoors (*n*-alkanes, PAHs) and indoors (phthalate esters, flame retardants), hospital interiors host several emerging organic contaminants (EOCs) recognized as potentially toxic as able to promote eye, skin and throat irritation, asthma, allergies, DNA mutations, endocrine disruption, cardiac and body temperature alteration, etc. Among them, there are psychotropic substances, drugs, fragrances and personal care chemicals, biocides and plasticizer. Nevertheless, investigations are overall restricted to macro-pollutants (NO, NO_2, PM, O_3, CO, SO_2) and sometimes to VOC characterization (including anesthetics) [1, 2].

The occurrence of organic contaminants was investigated in deposition dusts from interiors of Rome hospitals. Attention has paid to PAHs (as regular tracers of toxicity) and phthalates, as well as to licit and illicit drugs (nicotine, caffeine, cocaine, Δ^9-THC and cannabinol), pharmaceuticals and related chemicals (bisphenol-A, nonylphenols). Experiments were undertaken also in a dwelling home and outdoors, to enjoy of a reference environmental situation.

Despite most EOCs exist also in the gas phase, depositions are ascertained to hold more semi-volatile organics than fine airborne particulates. Besides, in interiors the human intake of toxicants via ingestion and skin contact is more important than outdoors; therefore, chemical characterization of dusts looks as a suitable preliminary approach in studies aimed at assessing the exposure and health risk for humans in hospitals.

[1] G. A. Eiceman, D. B. Shoff, C. S. Harden, A. P. Snyder, P. M. Martinez, M. E. Fleischer, and M. L. Watkins, *Anal. Chem.*, **1989**, *61*, 1093-1099.
[2] A. Kenarkoohi, Z. Noorimotlagh, S. Falahi, A. Amarloei, S.A. Mirzaee, I. Pakzad, E. Bastani, *Sci. Total Environ.*, **2020**, *748*, 141324.

Characterization of textile fibers by means of analytical pyrolysis coupled to mass spectrometry

Tommaso Nacci[a], Deborah Roversi[a], Francesca Sabatini[a], Ilaria Degano[a], Francesca Modugno[a]

[a] *Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa;*

Synthetic textiles are constituents of a variety of heritage objects and garments that are part of museum and archive collections. Such objects and garments present unprecedented and specific conservation challenges that need to be addressed in order to properly manage the collections and grant their accessibility to the future generations. To achieve such goal, effective analytical tools are required, capable to characterize modern and contemporary multi component polymeric materials in heritage objects, and to investigate risk factors and causes of degradation.

Spectroscopic techniques are widely employed for the characterization of textile fibers, due to the great deal of information that can be obtained, and the possibility to design portable instrumentations enabling in-situ analyses [1]. Polymer identification often relies on non-invasive and non-destructive spectroscopic tools, such as Raman and Attenuated Total Reflectance Fourier Transform infrared (ATR-FTIR) spectroscopies [2, 3]. However, these techniques are limited to a superficial analysis of the samples, preventing information on the bulk to be obtained.

Evolved Gas Analysis coupled to Mass Spectrometry (EGA-MS) and multi-shot Pyrolysis coupled to Gas Chromatography and Mass Spectrometry (Py-GC/MS) are emerging analytical methods for the study of synthetic polymers [4], but their applications on textile fibers are limited so far [5, 6]. The main advantages of these techniques are related to their capability to discriminate and characterize different fractions of composite samples, and to the small amount of textile fibers required for the analysis, making them suitable for investigating heritage objects. During EGA-MS analysis, the sample is subjected to a programmed heating and the gases evolved are analysed by the mass spectrometer. This technique provides useful compositional information by correlating specific thermal regions with the corresponding average mass spectra. Instead, in Py-GC/MS the sample is introduced in a micro-furnace and flash pyrolyzed at a certain temperature. The produced pyrolysis products are then separated on a gas-chromatographic column and revealed by the mass spectrometer. It is also possible to pyrolyze the same sample multiple times at different temperatures in order to characterize different fractions.

The present work aims at characterizing textile samples collected from high fashion garments and stage costumes dating 60s and 70s, to identify the chemical composition of the fibers used for their manufacturing. A set of reference textiles was also analyzed by ATR-FTIR, EGA-MS, and Py-GC/MS. The analytical approach allowed us to disclose the composition of the costumes constituted by synthetic and artificial fibers. The results collected on these multi-material heritage objects were fundamental to fine-tune an effective conservation aimed at removing or minimizing the damages due to ageing or poor preservation conditions, and to inform preventive conservation and exhibition strategies.

[1] P. Prego, C. Garcia-Ruiz, *Appl. Spectrosc. Rev*. **2016**, *51*, 258-281.
[2] P. Peets, I. Leito, J. Pelt, S. Vahur, *Spectrochimic. Acta A*. **2017**, *173*, 175-181.
[3] J. Miller, E. Bartick, *Appl. Spectroscop*. **2001**, *55*, 1729-1732.
[4] L.M. Lund, P.M.L. Sandercock, G.J. Basara, C.C. Austin, *J. Anal. Appl. Pyrol*. **2008**, *82*, 129-133.
[5] F. Sabatini, T. Nacci, I. Degano, M.P. Colombini, *J. Anal. Appl. Pyrol*. **2018**, *135*, 111-121.
[6] S. O'Brien, E. Okoffo, J. O'Brien, F. Ribeiro, X. Wang, S. Wright, S. Samanipour, C. Rauert, T. Toapanta, R. Albarracin, K. Thomas, *Sci. Total Environ*. **2020**, *747*, 141175.

Affinity of geopolymer based ion-exchange media for glyphosate in water matrices

Michele Castiglioni[1*], *Luca Rivoira*[1], *Irene Ingrando*[1], *Stefano Calanni*[1], *Karine Goulart*[2], *Renata Botti*[2], *Giorgia Franchin*[2], *Paolo Colombo*[2], *Maria Concetta Bruzzoniti*[1]

[1]*Chemistry Department, Università degli Studi di Torino, Via Pietro Giuria 7, 10125, Torino, Italy*
[2]*Industrial Engineering Dept. University of Padova, Via Marzolo 9, 35131, Padova, Italy*

michele.castiglioni@unito.it

Geopolymers (GPs) are aluminosilicate-based materials, characterized by -Si-O-Al-O- chains. Because of their green properties (i.e. low temperatures synthesis, industrial and agricultural waste feedstocks, etc.) and excellent physicochemical properties (i.e. high mechanical strength, resistance to low and high temperatures, etc.), GPs can be considered as adsorbents for environmental friendly applications, such as the removal of pollutants from waters.

Moving from the above-mentioned assumptions, in this work, adsorption properties of several GPs, characterized by different shapes and structures, towards glyphosate (a well-known herbicide with toxic effects against environment and human beings) in water matrices are presented.

To highlight the possible interaction mechanisms, the contribution of selected synthesis parameters was investigated, in particular: i) GPs shape, testing both powdered and 3-dimensional printed supports; ii) functionalization with specific agents, that were supposed to enhance the interaction towards glyphosate (i.e. magnetite, zeolites and commercial activated carbons with anion-exchange properties, etc.); iii) interaction with templating agents employed for the synthesis or the printing (e.g. bentonite and PEG1000).

Aliquots of 0.2 g of each material were put in contact with 50 mL of 2 mg/L glyphosate solution, analysing the residual concentrations by means of ion exchange chromatography coupled with suppressed conductivity detection.

Results showed that 3D-printed GPs have good adsorption performances towards glyphosate (removal rates up to 45% for sorbents modified with both active carbons and zeolite), as well as for GPs doped with magnetite nanoparticles (58%). The higher interaction obtained using magnetite doped GPs was ascribed to the selective complexation of Fe atoms with the phosphate group of the herbicide.

On the contrary, a negative effect of printing agents in particular for sodium bentonite was demonstrated since they reduce the adsorption capacities of 3D GPs of about 15%, tentatively ascribed to an obstruction in the sorbent reticulate.

This study confirms the affinity of 3D printed shape GP sorbents towards glyphosate; their potential use for water treatments is encouraged by their limited backpressure in respect to powder systems.

Aknowledgments

Financial support from Ministero dell'Università e della Ricerca, (PRIN call 2017: Nanostructured Porous Ceramics for Environmental and Energy Applications) is gratefully acknowledged.

Priority organic compounds in mussels and sediments from the Mar Piccolo of Taranto (Ionian Sea, Southern Italy)

S. Giandomenico[a], A. Di Leo[a], L. Spada[a], M. Calò[a], G. Bagnuolo[b], R. Ciannarella[b], M. Mali[c], G. Mascolo[b]

[a] CNR - Water Research Institute, via Roma 3, 74123 Taranto, Italy; [b]CNR - Water Research Institute, Via F. DeBlasio 5, 70132 Bari, Italy; [c]DICATECh - Polytechnic University of Bari, via Orabona 4, 70125 Bari, Italy

Human activities and the development of organic chemical industries led to an increased production of a large number of anthropogenic chemicals, such as priority organic compounds including polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs). Some of them are specially synthesized compounds for industrial application like polybrominated diphenyl ethers (PBDEs) or polychlorinated biphenyls (PCBs), other are unwanted by-products of chemical and mainly combustion processes such as polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs). Due to their persistence in the environment and lipophilic characteristics, they bioaccumulate in fat tissues, especially in those animals, as marine organisms, which show low metabolic capability.

The aim of this study was to examined the occurrence and distribution of EPA priority PAHs, 19 PCBs (marker and dioxin-like PCBs), 17 PCDD/Fs and 4 PBDE in transplanted mussels (active Mussel Watch) and sediments from the Mar Piccolo of Taranto (Ionian Sea, Southern Italy) a typical polluted semi-enclosed area of the Mediterranean Sea influenced by the near industrial site, urbanization, harbor activities, aquaculture and commercial fishing [1].

Mussel Watch strategy is feasible for biomonitoring in coastal and estuarine zone. Filter feeding bivalves process large volumes of seawater and are known to accumulate some organic contaminants to high concentrations in their tissues and in proportion to the degree of environmental contamination. This methodology consists of mussel transplantation from no impacted areas to selected coastal areas, characterized by potential impact. In this study mussels *Mytilus galloprovincialis* were put into cages suspended, in the selected site, at 7 m depth and 2 m away from the bottom for about 70 days.

During the exposition period, the uptake of pollutants was significant especially for PCBs: after 20 days, bivalves had accumulated significant amounts of these compounds equal to the 50 % of the value reached at end of experiment. After about 60 days, only PCBs concentrations in mussels didn't appear to reach steady-state values and their concentrations reached levels that exceed limits set by the European Community for food and foodstuff.

PCDD/Fs-dioxin like PCBs and total PCBs analyzed in these sediments, also exceed the highest chemical level of reference defined by the Italian Ministerial Decree 173/2016 for marine-coastal areas. In according with previous study, chlorinated compounds represent the most important and widespread source of contamination in the Mar Piccolo [2, 3]. Consequently, even after decades of banning and use restrictions, the PCBs pollutants are still the main issue in this basin.

Reducing these compounds is necessary and urgent to safeguard marine ecosystem, human health and, not less important, mussel farming, in the Taranto area.

[1] N. Cardellicchio, C. Annicchiarico, A. Di Leo, S. Giandomenico, L. Spada, Environ. *Sci. Pollut. Res*. **2016**, 23, 12495.

[2] N. Cardellicchio A. Buccolieri, A. Di Leo, S. Giandomenico, L. Lopez, F. Pizzulli, L. Spada *Mar. Pollut. Bull.* **2007** 55, 451.

[3] ISPRA **2010**.

Determination of metals in species of commercial interest from marine wetlands, coastal and offshore areas influenced by Po River outflows

Elena Sarti [a], Valentina Costa [a], Antonella Pagnoni [a], Cinzia Fabbro [b], Tommaso Diociaiuti [b], Luisa Pasti [a]

[a] *Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, via L. Borsari 46, 44121 Ferrara (ITALY)*

[b] *Division of Oceanography, National Institute of Oceanography and Applied Geophysics (OGS), via A. Piccard 54, 34151 Trieste (ITALY)*

The impact of heavy metal pollution on estuaries and coastal environments is a matter of major concern worldwide because of their persistency and tendency to bioaccumulate in the aquatic ecosystems, in addition to their toxicity [1]. These elements can derive from natural sources, influenced by bedrock geology of the drainage catchment and by weathering. However, along the Italian Northern Adriatic coast, anthropogenic pressure, in particular agriculture, industrial and municipal discharges, significantly increased the naturally occurring amounts of metals in the aquatic environment [2]. At the same time, Po delta and neighboring areas are traditionally exploited for fishery and mollusks farming, providing many species commonly used in Italian diet.

In this context, the aim of this study is to evaluate the concentration of several metals (Hg, As, Cd, V, Cr, Mn, Fe, Ni, Cu, Zn, Ba, Pb) in five marine species of commercial interest collected in different environments influenced by Po River outflow. Farmed mollusks come from both wetland (*Tapes philippinarum*) and coastal areas (*Chamelea gallina*), while native mussels (*Mytilus galloprovincialis*) and fish species (*Solea solea* and *Squalus acanthias*) were caught offshore. All species were sampled twice between 2018 and 2019. Furthermore, the metal content was measured also in surface sediments, to assess the environmental contamination of farming and capture areas.

The analytical determination was carried out by different atomic spectroscopy techniques, which were selected based on their analytical figure of merit. In detail, graphite furnace atomic absorption, cold vapor atomic absorption spectrometry (mercury analyzer), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and mass spectrometry (ICP-MS) were employed. Certified Reference Materials (CRMs) were employed for quality control purposes.

The results highlighted a correlation between the environmental state of the sites and metals content in the selected samples. The metals distribution in sediments were compared with the lithogenic composition, to attempt to discriminate between natural and anthropic input sources. In addition, the concentrations found in the selected marine species were correlated with those in surface sediments, thus confirming the tendency to bioaccumulate of heavy metals.

Finally, contamination levels of hazardous metals in sediments and biota were compared with Environmental Quality Standard (EQS) and threshold levels (TL) for human health.

[1] H. Fan, S. Chen, Z. Li, P. Liu, C. Xu, X. Yang, *Marine Pollution Bulletin* **2020**, *151*, 110864

[2] O. Bajt, A. Ramšak, V. Milun, B. Andral, G. Romanelli, A. Scarpato, M. Mitrić, T. Kupusović, Z. Kljajić, M. Angelidis, A. Çullaj, F. Galgani, *Marine Pollution Bulletin* **2019**, *141*, 283-298

Effects of different cooking methods in edible marine organisms: evaluation of fatty acids, polycyclic aromatic hydrocarbons and human risks arising from their consumption

S. Giandomenico[a]*, M. Nigro*[b]*, Ermelinda Prato*[a]*, I. Parlapiano*[a]*, L. Spada*[a,]*, F. Biandolino*[a]

[a] *CNR - Water Research Institute, via Roma 3, 74123 Taranto,* [b]*Università Carlo BO, via A. Saffi2, 61029 Urbino.*

Fish products are extremely important in human nutrition for their nutritional benefits due to the high content of n-3 polyunsaturated fatty acids (PUFAs) (Prato et. al. 2012). Therefore, they provide a healthy alternative to traditional meat consumption.

These products are cooked to improve their organoleptic properties as well as to make them healthier, but, cooking processes can alter the nutritional value of food (Ghribi et. al. 2017) and affect the development of unhealthy compounds, such as polycyclic aromatic hydrocarbons (PAHs), ubiquitous pollutants resulting mainly from combustion processes of organic material (Rose et. al. 2015).

The aim of this research is to provide information on the lipid content and fatty acids composition, with a focus on n-3 PUFAs, such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) and on PAHs in mussels (*Mytilus galloprovincialis*) and fish (*Trachurus trachurus*), before and after cooking processes (grilling, baking, microwaving, boiling and frying).

The lipid fraction in the samples was obtained through Folch's gravimetric method (1956) and the fatty acid profile - after trans-esterification - was determined by gas chromatography combined with a flame ionization detector (GC-FID). As for PAHs, after microwave-assisted solvent extraction (MASE), samples were cleared by size-exclusion chromatography (GPC) and determined by gas chromatography combined with mass spectrometry (GC-MS).

The results showed a highly significant increase in lipid content and n-6 PUFAs concentration through frying. Baking also brought about significant changes in the fatty acid profile of the samples, with an increase in saturated fatty acids and n-3 PUFAs. Considering that in Italy people eat about 12 g/day of shellfish and 30 g/day of fish, based on the data of this research, a person would consume an amount of EPA + DHA below the recommended intake (250-500 mg/day), in a range of 80 mg/day (fresh fish) - 174 mg/day (4 cm charcoal grill).

As for PAHs in fresh samples, mussels showed higher concentrations than fish. These data confirm that fish do not bioaccumulate these compounds like bivalves (Varanasi et. al. 1995). However, the levels in both species were below the limits set by EU Regulation 835/2011, which defines the maximum levels of contaminants in food. Charcoal grilling at the shortest distance from the heat source was found to be the cooking method with the most significant contribution of PAHs in both species. In mussels, compounds such as benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene and chrysene, which are considered human carcinogenic PAH markers, reached a content more than twice higher than in fresh food.

[1] E. Prato, F. Biandolino, *Food Chemistry*. **2012**, *131*, 1233-1239.

[2] F. Ghribi, S. Bejaoui, I. Rabeh, F. Aouini, I. Chetoui, M. El Cafsi, *Journal of Aquatic Food Product Technology*. **2017**, *26*, 1324-1336.

[3] M. Rose, J. Holland, A. Dowding, S.R. Petch, S. White, A. Fernandes, D. Mortimer, *Food and Chemical Toxicology*. **2015**, *78*, 1-9.

[4] U. Varanasi, J.P. Meador, J.E. Stein, W.L. Reichert, *Rev. Environ. Contam. Toxicol*. **1995**, *143*, 79-165

Occurrence of endocrine-disrupting compounds in water, treatment technologies and human exposure

A. Faggiano[a], M. Ricciardi[b], C. Pironti[b], O. Motta[b], Y. Miele[a], A. Fiorentino[a], A. Proto[a], L. Montano[c,d]

[a] Department of Chemistry and Biology, University of Salerno, via Giovanni Paolo II, 132-84084 Fisciano, Italy); [b] Department of Medicine Surgery and Dentistry "Scuola Medica Salernitana", University of Salerno, via S. Allende, 84081 Baronissi, Italy; [c] Andrology Unit and Service of Lifestyle Medicine in Uro-Andrology, Local Health Authority (ASL) Salerno, EcoFoodFertility Project, Coordination Unit, Oliveto Citra, via M. Clemente, 84020 Oliveto Citra, Italy; [d] PhD Program in Evolutionary Biology and Ecology, Department of Biology, University of Rome "Tor Vergata", via della Ricerca Scientifica 1, 00133 Rome, Italy.

Endocrine-disrupting compounds (EDCs) are xenobiotics chemicals that can bind to the body's endocrine receptors to activate, block, or alter natural hormone synthesis and degradation, thus increasing or inhibiting the normal endocrine function [1]. Both natural substances (hormones such as estrone, 17β-estradiol, and estriol) and synthetic chemicals (pesticides, pharmaceuticals, phthalates, bisphenol A, etc.) fall into this category [2]. In the last years, EDCs have accumulated in the aquatic environment through different pathways and sources as wastewater treatment plants, pharmaceutical and hospital waste, leaching of pesticide and other chemicals from industries and houses (Figure 1).

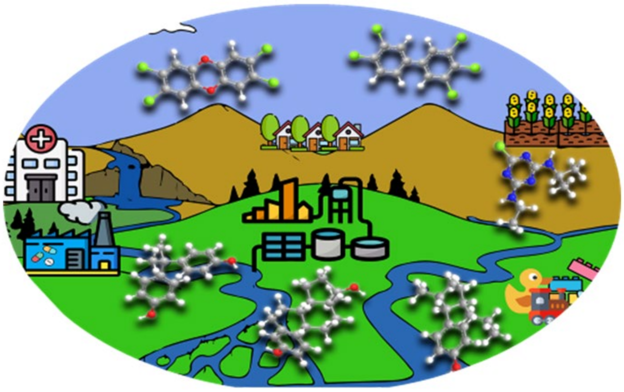


Figure 1. Source and path of endocrine-disrupting compounds into the water compartment.

In this work we report EDC occurrence in the aquatic compartment, main analytical methods used for their detection and quantification, treatment technologies for their removal from water and human exposure to them. Some EDCs as hormones, phthalates, alkyl phenols and bisphenol A are almost ubiquitous in significant amount in all the water matrices, including drinking water, suggesting that they can easily enter human body [3]. Moreover, many works correlate human exposure to high concentrations of these compounds with health issues as thyroid dysfunction, infertility, obesity and diabetes. However, studies on a wider number of subjects exposed to low doses of EDCs for longer times are needed to confirm the hypothesized causal relationship between EDC exposure and endocrine diseases.

[1] R.T Zoeller, T.R. Brown, L.L. Doan, A.C. Gore, N.E. Skakkebaek, A.M. Soto, T.J. Woodruff, F.S.V. Saal, *Endocrinology* **2012**, *153*, 4097–4110.
[2] A.C. Gore, D. Crews, L.L. Doan, M. La Merrill, H. Patisaul, A. Zota, *Endocr. Soc. J.* **2014**, *99*, 21–22.
[3] Y. Wan, T.M. Tran, V.T. Nguyen, A. Wang, J. Wang, K. Kannan, *Sci. Total. Environ.* **2021**, *750*, 141507.

Microplastic pollution and human exposure

M. Ricciardi[a]*, C. Pironti*[a]*, O. Motta*[a]*, Y. Miele*[b]*, A. Faggiano*[b]*, A. Proto*[b]*, L. Montano*[c,d]

[a] *Department of Medicine Surgery and Dentistry "Scuola Medica Salernitana", University of Salerno, via S. Allende, 84081 Baronissi, Italy;* [b] *Department of Chemistry and Biology, University of Salerno, via Giovanni Paolo II, 132-84084 Fisciano, Italy);* [c] *Andrology Unit and Service of Lifestyle Medicine in Uro-Andrology, Local Health Authority (ASL) Salerno, EcoFoodFertility Project, Coordination Unit, Oliveto Citra, via M. Clemente, 84020 Oliveto Citra, Italy;* [d] *PhD Program in Evolutionary Biology and Ecology, Department of Biology, University of Rome "Tor Vergata", via della Ricerca Scientifica 1, 00133 Rome, Italy.*

In the last years, the number of studies on microplastic (MP) pollution has grown quickly due to the potential risks for human health associated with human exposure. The high consumption of single-use plastic (face masks, gloves, gowns, food packaging, etc.) due to the COVID- 19 pandemic is leading to an increase in plastic and microplastic pollution in the future. The term microplastic is used to indicate plastic particles with a diameter lower than 5 mm [1]. Moreover, based on their origin, microplastics can be classified as primary (intentionally manufactured particles as microbeads, cleaning agents, coatings, paints, etc.) or secondary (derived from the deterioration of larger plastics during utilization or after discarding) [2].

Microplastics reach the environment through various routes such as improper disposal of plastic waste, industrial and domestic discharge, atmospheric transport, wet and dry deposition, use of sewage sludge and plastic mulching in agricultural land (Figure 1).

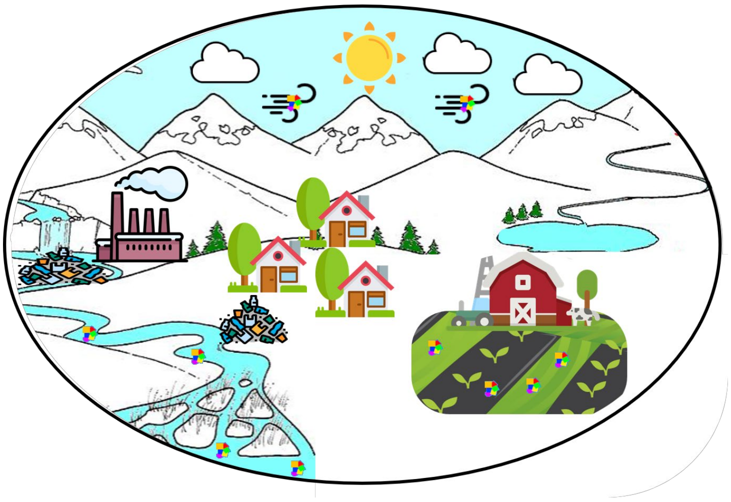


Figure 1. Source and path of microplastics into the environment.

The present work concerns occurrence and accumulation of MP on the environment from water (sea, river, lake, wastewater and drinking water) to soil and air. Moreover, the analytical methods used for their detection and quantification, their transport to humans and consequent effects on human health were analyzed. The human body's exposure to microplastics occurs through ingestion (intake of seafood, drinking water and fruits), inhalation and dermal contact [3]. High microplastic concentrations were detected in all the considered environmental matrices (water, air and soil), thus these exposure routes can represent important issues for human health.

[1] R.C Hale, M.E. Seeley, M.J. La Guardia, L. Mai, E.Y. Zeng, *J. Geophys. Res. Oceans* **2020**,*125*.
[2] M. Cole, P. Lindeque, C. Halsband, T.S. Galloway, *Mar. Pollut. Bull.* **2011**, *62*, 2588–2597.
[3] J.C. Prata, J.P. da Costa, I. Lopes, A.C. Duarte, T. Rocha-Santos, Sci. Total Environ. **2020**, *702*.

New *in silico* tools for the prediction of *in vitro* biotransformation in mammals

Ester Papa, Linda Bertato, Ilaria Casartelli and Nicola Chirico

Dipartimento di Scienze Teoriche e Applicate, Università degli Studi dell'Insubria, via Dunant 3, 21100 Varese, Italia

In silico models based on Quantitative Structure Activity Relationships (QSAR), are useful tools to support chemical risk assessment procedures, and represent valid alternatives to animal testing.

This study summarizes the main results obtained by our research group for the development, validation, and application of QSAR models in the context of the CEFIC-LRI ECO44 project [1]. This project is focused on the integration of multiple toxicokinetic parameters quantified *in vivo, in vitro and in silico*, which can be used for the quantification of bioaccumulation and toxicity in the context of chemicals risk assessment. This project led to the development of more than 100 models for the prediction of biotransformation in terms of intrinsic hepatic clearance measured *in vitro* ($CL_{in\ vitro,\ int}$), in human and murine hepatocytes and microsomal subcellular fractions, for over 10,000 organic molecules. The structure of the molecules included in the dataset, annotated in the form of SMILES strings, was used for the calculation of the theoretical molecular descriptors necessary for the construction of the QSAR models. Furthermore, the SMILES were used as input for the SMARTCyp software (v.3.1.0) [2] to predict the four molecular sites most subject to metabolism mediated by Cytochrome P450 (CYP-450), and the related reactions.

The multiple linear regression (MLR) QSAR models developed in this study were obtained using the ordinary least squares (OLS) method. The quality of the models was assessed according to the OECD guidelines [3], which are aimed at ensuring the statistical validity and transparency of QSAR models. In this regard, a QMRF document (QSAR Model Reporting Format) was created for each model developed in this study. QMRFs are necessary to support the use of QSAR models in the regulatory context. Finally, the two free software "QSARINS-Chem ECO44" and "IVBP-Suite" were specifically created to facilitate the application of the ECO44 models as well as to collect the related QMRFs.

[1] CEFIC-LRI ECO44 (2018-2021) A Toxicokinetic mammalian modelling framework for bioaccumulation assessment. http://cefic-lri.org/projects/eco44-a-toxicokinetic-mammalian-modelling-framework-for-b-assessment/

[2] Rydberg P, Gloriam DE, Zaretzki J, et al. *ACS Medicinal Chemistry Letters* **2010**, *1,* 96-100.

[3] OECD, (2004) Principles for the validation, for regulatory purposes, of (Quantitative) Structure-Activity Relationship models, OECD Publishing (Paris).

Evolution of $Cd_{1-x}Zn_xS$ pigments structure and morphology during wet and dry synthesis

Elena Castagnotto, Emanuela Sartori, Federico Locardi, Maurizio Ferretti

Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso, 31, 16146 Genova, Italy
**elena.castagnotto@edu.unige.it*

$Cd_{1-x}Zn_xS$ solid solutions have been used as pigments since the 1840s, with a breakthrough after 1920, thanks to the excellent chromatic properties. They were historically produced by means of either a dry or a wet process [1-4], producing, respectively, hexagonal or cubic (Cd,Zn)S. Side products such as amorphous or nano phases are likey to be formed during either synthesis. Pigment morphology and structure greatly influence the overall stability of the pigment; paintings in which these pigments are employed show remarkable signs of degradation after limited time periods.

Different experiments have been performed to understand the different outcomes of the original pigment synthesis methods and consequently study the stability of the forms obtained. Pigments with progressive substitution of Cd were synthesized by adapting the procedures described in early literature, modulating the final hue and obtaining a complete series from deep orange to light yellow. The samples were then characterized by means of XRF, XRD, SEM, TEM, Reflectance Spectroscopy and PL, following the different steps of production. $Cd_{1-x}Zn_xS$ was obtained with different crystal structure and size, having the double sulphate coexist with either CdS or ZnS. While sets of pigments can show same colour and elemental composition, the other properties are very different, changing greatly depending on time and temperature of the calcining process. Where Reflectance Spectroscopy and XRF are not capable of distinguish between different structures, luminescence has better results. Future work will proceed to correlate the degradation pathways of every pigment produced to a set of optical and elemental properties; the information gathered can be useful to develop a method for diagnostic identification based on non-invasive analysis able not only to identify the presence of $Cd_{1-x}Zn_xS$ pigments, but also their type and thus their predisposition to degradation.

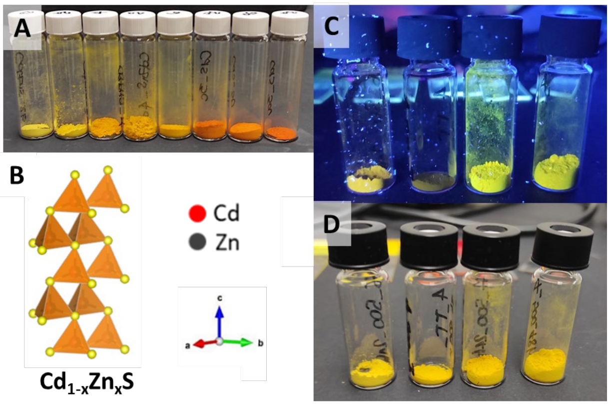


Figure. (A) Pigments obtained from yellow to orange; (B) $Cd_{1-x}Zn_xS$ crystal structure; (C) and (D) Sample subjected to different thermal treatment under UV light (365 nm) and natural light, respectively.

[1] I. Fiedler, M.A. Bayard, Cadmium Yellows, Oranges and Reds, (1986) 65-108.
[2] P. Dunning, Cadmium Pigments, High Perform. Pigment. Second Ed. (2009) 13–26.
[3] Feller, R. L. et al., Artists' pigments: a handbook of their history and characteristics, v. 1., (1997).
[4] J.R. Barnett, S. Miller, Opt. Laser Technol. 38 (2006) 445–453.

Dyes for a puppeteer: spectroscopic investigation of the materials in traditional Indian puppets

Alessandro Ciccola [a], *Ilaria Serafini* [a], *Adele Bosi* [a,b], *Giulia D'Agostino* [c], *Belinda Giambra* [d], *Maurizio Bruno* [c], *Paolo Postorino* [e], *Roberta Curini* [a]

[a] Dept. of Chemistry, [b] Dept. of Earth Sciences, e) Dept. of Physics, Sapienza University of Rome, Italy; c) Department of Biological, Chemical and Pharmaceutical Sciences and Technologies, [d] Cultural Heritage restore, University of Palermo

Tholu Bommalata (literally "dance of leather puppets") is the traditional shadow theatre of the Telugu Indian states of Andhra Pradesh, Telangana and Karnataka. During the show, puppeteers press the dolls behind a backlit screen, so the audience can only see dancing shadows [1]. Dolls can be moved from anyone, but only a skillful *sutradhar* (literally "wire mover") can give them life. He is the leader of a familiar-run troupe, where everyone has a specific role: dancer, singer, narrator and actor [2]. Every puppet is made from leather whose origin was not arbitrary (deer to represent Gods, goat for saints or common people, buffalo for demons), while today goat skin is the most used. Dolls are charged of an enormous spiritual value. Today, *Tholu Bommalata* is a a dying art, whose decline is evident. Fifty years ago, more than one hundred-eighty troupes were active in thirty different Indian districts; today there are only nine.

In this study, two Tholu Bommalu, made in 1978 by Ramana Murthy theatre and part of a one hundred-seventythree artifacts collection stored at the International Puppets Museum "Antonio Pasqualino" in Palermo, Sicily, Italy, were characterized in order to obtain information related to the use of dyes. To this aim, a complete spectroscopic approach was used: Visible Light Micro-Reflectance spectroscopy was used for the preliminary identification of the molecular class of dyes sampled on cotton swabs[3], while Surface Enhanced Raman Scattering spectroscopy for the identification of the specific dye[4]. Several synthetic dyes were identified, belonging to different typologies of compounds and resulting in an interesting overview of materials used in Tholu Bommalata manufacturing.

Acknowledgement

Authors thanks the Director of "Museo Internazionale delle Marionette Antonio Pasqualino", Palermo, for allowing and collaborating to the diagnostic campaign.

[1] A. Chandra Sekhar, A selected crafts of Andhra Pradesh, in: *Census India 1961* **1961**.
[2] D. Sarma, A. Homen, *Storytelling and Puppet Traditions of India* **2010**.
[3] C. Montagner, M. Bacci, S. Bracci, R. Freeman, M. Picollo, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2011,** *79*, 1669.
[4] C. Sessa, R. Weiss, R. Niessner, N.P. Ivleva, H. Stege, *Microchem. J.* **2018**, *138*, 209.

How metal-polymers interactions can affect the aesthetic features of protective coatings for artistic objects: the case of chitosan-based films

F. Boccaccini [a,b], C. Giuliani [b], C. Riccucci [b], M. Pascucci [b], G.M. Ingo [b], G. Di Carlo [b]

[a] Department of the Earth Sciences, Sapienza University of Rome, Piazzale Aldo Moro, 5, 00185 Rome, Italy;
[b] Institute for the Study of Nanostructured Materials (ISMN), National Research Council (CNR), Via Salaria km 29300, 00015 Monterotondo, Italy.

When new protective coatings for cultural heritage materials are developed, these need to be carefully validated on reference materials before the application on real artworks. Both protective properties and aesthetic requirements have to be satisfied when dealing with materials to be used on artistic objects.

An easy and time-saving method used to evaluate such features is to submit reference samples to accelerated ageing treatments and to compare through time the behaviour of both coated and uncoated surfaces. However, accelerated degradation tests, which duration is usually no longer than a few months, are not suitable to monitor the long-term coatings behaviour. Interactions between the substrate and the protective film, as well as chemical or physical degradation of this latter, can indeed occur after a period of time longer than the one investigated by the accelerated ageing treatments. Studying long-term effects that can potentially compromise the protective and aesthetic properties of the coatings is thus mandatory when new conservative materials are developed.

In this work, we propose an example of how short and long-lasting ageing tests might induce different treatment responses leading to an equivocal evaluation of the coating protective and aesthetic requirements. Chitosan-based coatings have been selected as green and eco-friendly materials for the protection of modern silver artifacts. They have been developed during the European Union's project NANORESTART [1] and previously tested on copper-based alloys with promising results [2, 3].

Here, two different coatings formulations have been applied on sterling silver reference substrates and subjected to distinct ageing tests. These have been developed to simulate both a short-time exposure to a highly polluted environment and a long-time conservation in a real-like storage box. Optical microscopy (OM), electron scanning microscopy coupled with an energy dispersive spectrometer (FE-SEM-EDS) and UV-vis spectroscopy have been used to investigate the coatings' physico-chemical properties, both before and after the tests. Differences in treatments' response are related to the occurrence of short or long-term interactions between the metal substrate, the chitosan-based coatings and the environmental aggressive species.

[1] H2020 NANORESTART project, "Nanomaterials for the restoration of works of art", Grant Agreement n. 646063, http://www.nanorestart.eu
[2] C. Giuliani, et al., *Progress in Organic Coatings*. **2018**, *122*, 138-146.
[3] M. Salzano de Luna, et al., *Angew. Chem. Int.* **2018**, *57*, 1-6.

Cadmium and other hazardous elements in phosphatic fertilizers in conformity to the new European Regulation 2019/1009

Maria Chiara Manghi[a], Elisabetta Peruzzi[b], Riccardo Calzavara[b], Pier Luigi Graziano[b], Bruno Pavoni[a], Mauro Masiol[a]

[a] Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari Venezia, via Torino 155, I-30172 Mestre Venezia, Italy
[b] Arvan s.r.l., via Gramsci 59, I-30034, Mira (VE), Italy

The current European Fertilizers Regulation EC n. 2003/2003 does not include any direction for the content in cadmium [1]. On 25 June 2019, the new EU Fertilizing Products and Amending Regulation (EU-FPR) 2019/1009 was promulgated by the European Parliament and the Council, fixing an initial and temporary limit for Cd content in inorganic macronutrient fertilizer to 60 $mg_{Cd} \cdot kg_{P_2O_5}^{-1}$ [2]. The new European limit for Cd would be the most stringent in the world and only 15% of the phosphorite deposits currently exploited exhibits a low cadmium content complying with the new standard once processed to fertilizer. Since there are no substitutes for phosphate rock in phosphatic fertilizer production [3,4], the outcome of the new standard application would make unsustainable the supply of phosphatic fertilizers. This will result in a short-term measure that goes beyond the long-term sustainability objective of the proposal. In addition, the new standard will inevitably and disproportionately penalise some producers, mainly from developing countries in North Africa. It is therefore important to investigate for Cd and other hazardous elements content in fertilizers used for food production. The present research has analysed a total of 41 samples of fertilizers both for hobby and professional use obtained from the Italian market. Producers of Western and Middle Eastern Europe use the same phosphorite deposits to obtain fertilizers, thus the results of this investigation can be extended to the whole area. Obtained samples were initially pulverized in a ball mill and subjected to acid digestion in a microwave oven. Different acid digestion methods (HNO_3 - HF - *aqua regia* - H_2O_2) were developed and tested for processing phosphate rock, inorganic and organo-mineral fertilizers to optimize the dissolution of different matrices. Standard reference materials, NIST SRM-695 (NPK fertilizer) and BCR-032 (Morocco phosphate rock), were processed using the same methods. Elemental analyses were performed in ICP-OES (Na, Mg, Al, Si, P, S, K, Ca, Fe, Se, Hg) and ICP-MS (Li, Be, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Sr, Cd, Sn, Sb, Ba, Tl, Pb, Bi, U). The first results showed very low Cd concentrations in hobby products. This commercial sector is known to import low-cost phosphate rock from Russia or Cola Peninsula, with a lower nutrient quality, but also a lower Cd content in comparison with professional products. Uranium content was found in relatively high concentrations and a radioactivity study has been considered as a logical extension of this research. The next analysis of more samples collected in spring will account for different fertilizer types used in distinct agricultural phases.

[1] European Union. *Off. J. Eur. Union*. **2003**, EUR-Lex - 32003R2003.
[2] European Union. *Off. J. Eur. Union*. **2019**, EUR-Lex - 32019R1009.
[3] Mar, S.S., Okazaki, M. *Microchem. J.* **2012**, 104, 17–21.
[4] Ulrich, A.E. *Sci. Total Environ*. **2019**, 650(1), 541–545.

FOOD WASTE from households

Massimiliano Boccarossa [1,2] *, Laura Manuritta* [1]*, Fabrizio Passarini* [1]*, Ivano Vassura* [1]

[1]*Department of Industrial Chemistry "Toso Montanari" and Interdepartmental Centre for Industrial Research in Renewable Resources, Environment, Sea and Energy – University of Bologna, v. D. Campana 71, Rimini, I-47922, Italy*
[2]*Environmental Protection Agency of Marche Region (ARPAM),*
via Barsanti 8, Pesaro, I-61122, Italy.

Analyzing the composition of municipal unsorted waste during the years shows that the organic fraction was often composed by a high percentage of food waste. So, for three years in the last waste composition analyses were applied a subcategory of organic waste represented by food waste. Applying the percentage of waste fractions founded in the analyzed samples, to the whole mass of waste can give an estimated value of the composition of the entire amount of waste generated in a studied area. The split between organic waste and food waste, in particular, can give information about the entire food waste of the investigated area / region.

Organic fraction is made up by fruit peels and fruit stones or meat bones for example and other inedible elements, instead waste is made up of food still in its wrapper, food recently expired or food slightly bruised (e.g. food covered with a (surface) mould layer), whole box or parts of unfinished meals.

Analyses consist in a manual separation of the waste sample in something more than twenty categories.

The weighted average percentage of food waste in the analyzed samples of unsorted waste returns a value of food wasted in landfills for the entire investigated area. Reporting the amount to the inhabitants served by this area landfill can give a per capita value of food waste in the un sorted waste.

The ratio between food waste and organic waste can returns a "food waste ratio" to be applied to the organic fraction separated collection, as to find the amount of food wasted in the specific separate collection. From the total amount it can be deduced the per capita for the area inhabitants.

The first investigated area correspond to the Marche Region (divided in the five provinces) but then, the calculation has been extended to the all nation, Italy.

The study as finally directed to the translation of the per capita and total values of food waste in GHG emission connected to this topic to estimate environmental and economic impacts related.

[1] P. Rossi, N. Bianchi, *Chem. Soc. Rev*.**2016**, *45*, 5455.

Agri-food waste derived materials for the removal of pollutants from water

M. Rigoletto[a], E. Gaggero[a], C. Noè[b], E. Laurenti[a], P. Calza[a], M. Sangermano[b]

[a] Department of Chemistry, University of Torino, Via Pietro Giuria 7, 10125 Torino, Italy;
[b] Department of Applied Science and Technology, Politecnico di Torino, C.so Duca degli Abruzzi 24, Torino, 10129, Italy.

In recent years, circular economy approach and the research for innovative uses for waste materials are becoming increasingly important. This also includes new strategies for the recovery of large quantities of agri-food waste deriving from agricultural activities or from the preparation and consumption of food. Often this waste is landfilled or burned, contributing to increase environmental hazards, but it should be considered as a potential raw material due to its high content in lignocellulosic biomass. Indeed, crop residues are an interesting source of cellulose, hemicellulose, lignin, sugar and some extractives and their valorization is even more studied [1].

Lignocellulosic biomasses contain natural polymers with several functional groups, such as hydroxyl, carbonyl, carboxyl, methoxy, sulfhydryl, ether, or amino groups, that can be involved in complexation, chelation and adsorption processes. Therefore, the use of lignocellulosic biomass constitutes an interesting source of useful materials and an alternative to the classic treatment for water decontamination.

In this study we report the results of recovery and modification of cellulose extracted from soybean hulls. Cellulose is the most abundant biopolymer on earth, and it is the main component of the hulls of soybeans, which are eliminated before grinding the seeds. The use of hulls *in toto* as adsorbents for water remediation has been previously demonstrated [2], but isolation of their components permits a wide range of employment and a modulation of relative properties through functionalization reactions. Therefore, cellulose has been isolated from the matrix by the procedure of Alemdar and Sain [3] consisting in three consecutive hydrolytic steps, respectively: basic (with NaOH 2% w/w), acid (with HCl 1M), and basic again (with NaOH 2% w/w). Then, after chemical-physical characterization, the product obtained has been used for *(i)* preparation of hydrogels by carboxymethylation [4] followed by methacrylation [5] and *(ii)* preparation of active cellulose fibers by functionalization with 3-aminopropyl-triethoxysilane. Preliminary results showed that both products are effective in the removal of organic and inorganic pollutants in water samples.

Acknowledgments - This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie SusWater grant agreement No 101007578.

[1] P. Rao, V. Rathod, *Chem. Rec.* **2019**, 19, 1858–1871
[2] M.L. Tummino, V. Tolardo, M. Malandrino, R. Sadraei, G. Magnacca, E. Laurenti, *Front. Chem.* **2020**, 8, 763.
[3] A. Alemdar, M. Sain, *Bioresour. Technol.*, **2008**, 99, 1664–1671
[4] P. J. Robles Barros et al., *Int. J. Biol. Macromol.*, **2020**, 144, 208–218
[5] C. Noè, C. Tonda-Turo, I. Carmagnola, M. Hakkarainen, M. Sangermano, *Coatings*, **2021**, 11, 127

The water-energy nexus in a regional drinking water supply system

Francesco Arfelli[a], *Luca Ciacci*[a], *Fabrizio Passarini*[a,b]

[a]*Department of Industrial Chemistry "Toso Montanari", University of Bologna, viale del Risorgimento 4, 40136 Bologna, Italy;* [b]*Interdepartmental Centre of Industrial Research "Renewable Resources, Environment, Sea and Energy", University of Bologna, via Angherà 22, 47922 Rimini, Italy.*

Water sustainability is a topic of global interest mainstreamed by the United Nations that, in the "2030 Agenda for Sustainable Development", inserted "Clean water and sanitation" between the 17 sustainable development goals [1]. The balance between water supply and demand implies the investment of resources aimed at optimizing the management of water sources and requires a detailed knowledge of the techniques and operations involved in a drinking water supply system (DWSS), meant as the set of withdrawal, treatment and distribution processes (Figure 1).

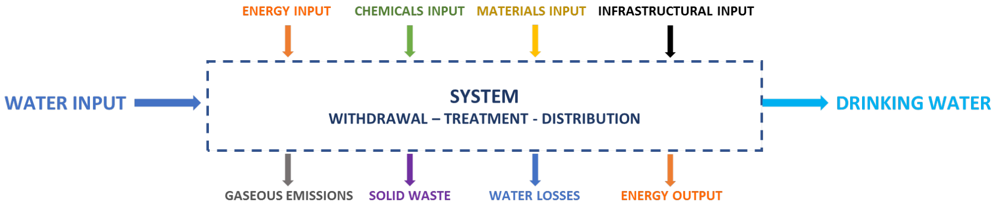


Figure 1: schematic representation of a drinking water supply system

Accordingly, the study consists in the application of the Life Cycle Assessment (LCA) methodology to the DWSS located in the Romagna territory, with the aim to analyze the system as a whole and to compare, from an environmental perspective, different production alternatives associated to three water sources (dam water, RD; surface water, SW; and groundwater, GW) and two treatment technologies (conventional and ultrafiltration). This work required a previous definition and quantification of the main water and energy flows through the Material Flow Analysis (MFA), allowing to identify the interlinkages and the reciprocal dependencies between the two resources in the local context. It is observed that, despite electricity is essential for drinking water production, the drinking water sector is responsible for a very limited portion of the regional energy consumption.

The impact assessment, calculated choosing 1m^3 as functional unit and following the ReCiPe 2016 method [2], despite the influence of the dam infrastructure, assigned the best comprehensive environmental performances to the drinking water deriving from RD and treated with the conventional technology. On the other side, both GW and SW, treated in conventional plants and SW, treated following the ultrafiltration process, resulted in higher impacts. The main contributors responsible for the observed values have been, in case of GW, the amount of electricity required to draw up water until the soil level and the aluminum sulfate employed in the treatment plants, while, in case of SW, the higher influence is given by the composition of filters and the electricity needed to pump water through their surface. Afterwards, it is confirmed that decreasing the dependency on electricity produced by fossil sources, the environmental impacts observed are remarkably reduced.

The LCA methodology, especially when accompanied by considerations about the *water-energy nexus,* is confirmed an essential tool to determine the environmental performances of processes that could significantly help and drive companies in addressing environmental-friendly solution in the field of water sustainability, which represents one of the most urgent challenges to face in the coming years.

[1] UN, "United nations general assembly," **2015**.

[2] M. A. J. Huijbregts *et al.*, *Int. J. Life Cycle Assess.*, **2017**, 138–147.

Società Chimica Italiana

SCI2021

CHIMICA ANALITICA (ANA)

- Orals
- Posters

New trends for the enrichment and liquid chromatography-mass spectrometry analysis of peptides with protein post-translational modifications

Susy Piovesana [a]

[a] *Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy*

Protein post-translational modifications (PTMs) are involved in important physiological and pathological processes occurring in biological systems. Some PTMs, mainly phosphorylation and glycosylation, are extensively investigated by proteomics, due to the availability of an array of analytical methods for their enrichment and characterization by LC-MS [1]. Among the most studied PTMs, protein phosphorylation is probably the best characterized one, for which there are many strategies suitable for the enrichment of phosphopeptides. Popular enrichment strategies rely on the affinity of phosphate moiety to metal cations and metal oxides, which is an efficient approach for the development of new materials for phosphopeptide enrichment before LC-MS analysis.

For several other PTMs, there is limited availability or complete lack of analytical methods, regardless of the potential biological significance. Such PTMs include tyrosine O-sulfation, which is an important PTM correlated to inflammation, virus infection, and signal pathways. Nevertheless, methods for the enrichment and characterization of sulfopeptides are currently based on lengthy derivatization protocols, or expensive antisulfothyrosine antibodies, although affinity chromatography, molecularly imprinted polymers, and weak anion exchange sorbents were also suggested for the purpose [2]. Moreover, sulfopeptides suffer from poor ionization and decomposition in conventional LC-MS instrumental setups used in proteomics, phenomena that in turn impede sulfopeptide detection and sulfate site localization. The differential analysis of sulfation and phosphorylation by MS is further complicated by the nearly isobaric nature of these modifications [1,2].

In this context, the talk will cover the development of enrichment methods for peptides with PTMs, starting from the enrichment of phosphopeptides, then moving to the neglected PTM sulfation. The covered strategies are based on affinity chromatography, which is suitable for both enrichment of phospho- and sulfopeptides. In the case of sulfopeptide analysis, the specific issues of sulfation will be covered and discussed with recent literature examples on the topic [3].

[1] L. Pieroni, F. Iavarone, A. Olianas, V. Greco, C. Desiderio, C. Martelli, B. Manconi, M.T. Sanna, I. Messana, M. Castagnola, T. Cabras, *J. Sep. Sci*. **2020**, *43*, 313.
[2] Y.S. Yang, C.C. Wang, B.H. Chen, Y.H. Hou, K.S. Hung, Y.C. Mao, *Molecules* **2015**, *20*, 2138.
[3] A.L. Capriotti, A. Cerrato, A. Laganà, C.M. Montone, S. Piovesana, R. Zenezini Chiozzi, C. Cavaliere. *Anal. Chem*. **2020**, *92*, 7964.

Organic Electrochemical Transistors as low cost chemical sensors

Erika Scavetta [a], *Isacco Gualandi* [a], *Federica Mariani* [a], *Danilo Arcangeli* [a], *Domenica Tonelli* [a], *Luca Possanzini* [b], *Francesco Decataldo* [b], *Marta Tessarolo* [b], *Beatrice Fraboni* [b]

[a] *Dipartimento di Chimica Industriale 'Toso Montanari', Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy (erika.scavetta2@unibo.it);* [b] *Dipartimento di Fisica e Astronomia, Università di Bologna, Viale Berti Pichat 6/2, 40127 Bologna, Italy*

Organic Electrochemical Transistors (OECTs) are promising electronic devices that have recently attracted increasing interest in the field of chemical sensors, since they exhibit intrinsic signal amplification, work without the need of a freestanding reference electrode, operate at low power (< 100 μW) and can be easily miniaturized and adapted to non-flat, flexible and even textile substrates. In addition, providing high sensitivity together with biocompatibility and low-cost, they have been proposed as analytical tools for the reliable detection of a wide range of low concentration analytes also in biological fluids.

This contribution aims at giving an overview of OECTs as chemical sensors, describing the most recent applications of such devices. Particular emphasis will be given to the description of all-poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) based OECTs. These devices, recently developed by our research group, are entirely made of PEDOT:PSS and can be therefore fabricated by using only one conductive material, with low cost and easily scalable procedures. All PEDOT:PSS OECTs can be used as sensors for the reliable detection of redox active analytes, such as ascorbic acid, dopamine, adrenaline or uric acid, which are able to undergo oxidation at PEDOT:PSS. The redox molecules react at the transistor elements (PEDOT:PSS gate or channel) affecting the electrochemical mechanisms that modulate the current flowing across the channel. Consequently, an increase in the analyte concentration can be correlated with a decrease of the absolute value of the channel current, which is used as the analytical signal [1].

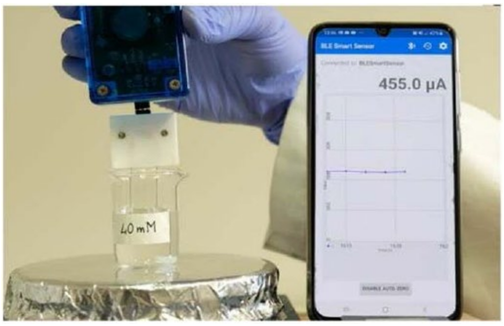


Fig. 1 Portable OECT sensor coupled to a portable electronic readout.

On the other hand, the selectivity issue must be addressed to allow the widespread use in real-life applications. To overcome this problem, two approaches can be proposed: (i) the functionalization of the gate electrode with chemical species able to selectively interact with the target analyte [2, 3] and (ii) a potentiodynamic approach based on the variation of the voltage applied to the gate electrode, to obtain a transconductance curve wherein the waves due to different redox active compounds can be resolved [4]. As far as the former strategy is concerned, glucose and lactate biosensors have been fabricated by immobilizing the enzymes glucose or lactate oxidase on the gate electrode surface. Moreover, pH or chloride sensors have been developed by entrapping iridium oxide or silver/silver chloride nanoparticles, respectively, in the PEDOT film. As regards the potentiodynamic approach, the detection of dopamine in the presence of ascorbic and uric acids has been described. In particular, the sensitivities and limit of detection obtained with the OECT sensor were comparable or even better than those achieved by amperometric techniques employing a conventional electrochemical setup.

[1] I. Gualandi, M. Marzocchi, E. Scavetta, M. Calienni, A. Bonfiglio, B. Fraboni, *J. Mater. Chem. B* **2015**, *3*, 6753; [2] I. Gualandi, M. Tessarolo, F. Mariani, D. Arcangeli, L. Possanzini, D. Tonelli, B. Fraboni, E. Scavetta, *Sensors* **2020**, *20*, 1; [3] I. Gualandi, M. Tessarolo, F. Mariani, T. Cramer, D. Tonelli, E. Scavetta, B. Fraboni, *Sens. Actuators B* **2018**, *273*, 834; [4] I. Gualandi, D. Tonelli, F. Mariani, E. Scavetta, M. Marzocchi, B. Fraboni, *Sci Rep* **2016**, *6*, 35419.

Graphene-based electrodes for the detection of biomarkers in sweat

Fabrizio Poletti,[a] Alessandra Scidà,[b] Barbara Zanfrognini,[b] Alessandro Kovtun,[b] Vitaliy Parkula,[b] Laura Favaretto,[b] Manuela Melucci,[b] Vincenzo Palermo,[b,c] Emanuele Treossi, [b] Chiara Zanardi [a,b]

[a]*Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Modena, Italy*
[b]*Institute for the Organic Synthesis and Photoreactivity, National Research Council, Bologna, Italy*
[c]*Chalmers University of Technology, Department of Industrial and Materials Science, Gothenburg, Sweden*

Wearable sensors, which accurately measure biomarkers of physiological interest, allow a more personalized approach to fitness goals and to health monitoring. Among different transduction mechanisms, the electrochemical one is characterised by high robustness and ease of use. The inclusion of carbon-nanosized materials impart the sensor peculiar properties, suitable for the effective detection of many species present in biological fluids.

In this talk, we will discuss the advantages in the use of graphene and related materials in the realization of electrochemical devices for the continuous monitoring of sweat. The active role played by oxidized moieties naturally present on carbon nanosheets are discussed by considering responses obtained from commercial screen printed electrodes chemically modified by graphene-based films [1,2].

Beside the use of conventional electrochemical substrates, we will also discuss the performance of novel electrochemical platforms entirely made of graphene. They are obtained starting from a flexible, electrically conductive, paper-like material, already used for electronic applications like NFC antennas [3]. Graphene papers can be shaped in different ways and stably flexed on plastic and textile supports, opening new possibilities in the development of smart fabrics. The performance of these innovative devices is compared with commercial electrode platforms made of bulk graphite.

[1] G. Maccaferri, C. Zanardi, Z. Y. Xia, A. Kovtun, A. Liscio, F. Terzi, V. Palermo, R. Seeber, *Carbon* **2017**, *120*, 165.
[2] F. Vulcano, A. Kovtun, C. Bettini, Z. Xia, A. Liscio, F. Terzi, A. Heras, A. Colina, B. Zanfrognini, M. Melucci, V. Palermo, C. Zanardi, *2D Materials*, **2020**, *7*, 024007.
[3] A. Scidà, S. Haque, E. Treossi, A. Robinson, S. Smerzi, S. Ravesi, S. Borini, V. Palermo, *Materials Today* **2018**, *21*, 223.

Allergenicity assessment of novel foods by identifying marker peptides using bioinformatics and LC-ESI-MS/MS

C. D. Calvano[1,2], M. Bianco[3], G. Ventura[3], L. Guadalupi[3], I. Losito[2,3], and T.R.I. Cataldi[2,3]
[1]Dipartimento di Farmacia-Scienze del Farmaco, [2]Centro interdipartimentale SMART, [3]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, via Orabona 4, 70126, Bari, Italy

One of the main priorities of Food 2030[1], the research and innovation policy framework from the European Commission, is to respond to the progressive growth of population realizing a more sustainable food system. There is an urgent need to provide safe and nutritious foods, not yet used for human consumption, obtaining adequate alternative proteins from genetic engineering approaches and novel food sources. One of the most difficult aspects of assessing the safety of foods derived from novel food proteins as algae and insects, is the allergenicity risk assessment. A likely approach applied to this aim is the use of bioinformatics to compare the sequences of a novel protein with those of known allergens. Within the last period several allergen databases have been set up collecting and archiving the current data of allergen sequences such as IUIS allergen (www. allergen.org), Allergome (http://www.allergome.org/), COMPARE (http://comparedatabase.org/), AllergenOnline (http://www.allergenonline.org), and ALLFam (http://www.meduniwien.ac.at/allfam/).

Traditionally, the primary sequence of a novel protein is compared with those of known allergens using a local alignment algorithm such as FASTA and a threshold value of 35% sequence identity over a sliding window of 80 amino acid (aa) residues has been set[2]. Primary sequence determination is usually performed by liquid chromatography (LC) coupled to mass spectrometry (MS) which has played a pivotal role in food allergen identification and characterization. The interplay between MS, proteomics and bioinformatics approaches can help in selecting certain motifs or peptides that may contribute to assess in silico allergenicity also for novel foods. Following bottom-up strategies, marker peptides[3] with inherent features, namely uniqueness for each protein, stability, absence of chemical modifications, no missed cleavages during enzymatic digestions, more than six amino acids in their sequence, and doubly/triply charged ions have been selected for common allergen food proteins as milk, nut, egg, crustaceous, fish.

In this communication, strengths, and weaknesses of generally employed proteomics strategies coupled to bioinformatics will be discuss for the qualitative determination of stable marker peptides, selected after in silico allergenicity evaluation, in native, spiked, incurred, and processed food products. Some applications to conventional or novel foods will be presented.

Acknowledgments

This work was supported by projects: (i) PONa3_00395/1 “BIOSCIENZE & SALUTE (B&H)” and (ii) Progetto di Ricerca di Interesse Nazionale-PRIN 2017YER72K- “*Development of novel DNA-based analytical platforms for the rapid, point-of-use quantification of multiple hidden allergens in food samples*”, financed by the Italian Ministero per l’Istruzione, l’Università e la Ricerca (MIUR).

References

[1] https://ec.europa.eu/knowledge4policy/publication/food-2030-innovative-eu-research-ensures-foodsystem-future-ready_en
[2] EFSA Panel on Dietetic Products, Nutrition, and Allergies (2016) Guidance on the reparation and presentation of an application for authorisation of a novel food in the context of regulation (EU). *EFSA J.* **2015**/2283, *14*, 4594.
[3] Pilolli, R.; Nitride, C.; Gillard, N.; Huet, A. C.; van Poucke, C.; de Loose, M.; Tranquet, O.; Larré, C.; Adel-Patient, K.; Bernard, H.; Mills, E. N. C.; Monaci, L. *Food Res. Int.* **2020**, *128* (October 2019), 108747.

Organic Pollutant Removal using Photo-Fenton Processes in the presence of Fe(III) complexing agents

Bianco Prevot Alessandra[a], *Bertolotti Silvia*[a], *Minella Marco*[a], *Laurenti Enzo*[a], *Brigante Marcello*[b], *Mailhot Gilles*[b].

[a] *Università degli Studi di Torino, Dipartimento di Chimica, via Pietro Giuria 7, 10125 Torino, Italy.*
[b] *Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, 63000 Clermont–Ferrand, France.*

Water resources of high quality are a premise for the development of a sustainable human society. The overuse of hydric resources and their incorrect management can abruptly affect the sustainability of our society on the long period.

Advanced Oxidation Processes (AOPs) allow the degradation of several organic compounds through the generation of reactive species and have been proposed as tertiary treatment in the presence of bio recalcitrant chemicals, as well as a viable approach for the removal of contaminants of emerging concerns (CECs), detected at trace and sub trace levels in natural water bodies.

Among AOPs, Photo-Fenton processes involve cheap and non-toxic reagents to produce highly oxidative species. They basically work in the presence of iron salts able to activate oxidants, typically hydrogen peroxide and recently also alternative species, e.g. peroxodisulphate, percarbonate and peroxymonosulphate. The optimum pH has been found to be 2.8 where the photoactive species $FeOH^{+2}$ has its maximum concentration, thus needing acidification and further neutralization of the water for the treatment and then for its disposal.

Based on this drawback, in the last year great efforts have been done to run efficient Photo-Fenton processes at milder pH values, mainly by exploiting the formation of photoactive iron complexes upon addition of suitable ligands. Moreover, heterogeneous Photo-Fenton has also been studied as a possible viable alternative. Photo-Fenton processes activated by Fe(III)-EDDS ([S,S']-ethylenediamine-N,N'-disuccinic acid) complexes have attracted huge attention, since they can be operated at circumneutral pH and because EDDS ligand is biodegradable [1].

It was also investigated an eventual synergistic contribution to the process by soybean peroxidase (SBP), a Fe(III)-heme containing glycoprotein that catalyzes the oxidation of organic and inorganic substrates by H_2O_2. Previous studies have shown that in heterogeneous systems containing SBP and a photocatalyst a synergistic mechanism is operative due to a better exploitation of the photo-formed H_2O_2 with an increased removal rate of water pollutants [2,3]. Since it has been reported the generation of H_2O_2 under irradiation of Fe(III)-EDDS, the effect of the contemporary presence of SBP and Fe(III)-EDDS on the removal of 4-chlorophenol from water solution was investigated.

The use of ligands, the activation of alternative oxidants instead of hydrogen peroxide as well as the addition of heterogeneous catalysts, open important questions involving analytical chemistry competences in a multidisciplinary context, concerning: the in depth assessment of the operating mechanism, the identification of the iron species present in different experimental conditions together with their photoactivity, the identification of reactive species generated, the comprehension of the fate of the added ligands and oxidants, together with the need of establishing the overall sustainability of the different approaches. All these aspects assume much relevance in the perspective of the application of the process to real cases.

[1] Y. Wu, M. Passananti, M. Brigante, W. Dong, G. Mailhot, Environ. *Sci. Pollut. Res.* **2014**, *21*, 2154.
[2] P. Calza, P. Avetta, G. Rubulotta, M. Sangermano, E. Laurenti, *Chem. Eng. J.* **2014,** *239*, 87.
[3] M. Sarro, N. P. Gule, E. Laurenti, R. Gamberini, M.C. Paganini, P.E. Mallon, P. Calza, *Chem. Eng. J.* **2018,** *334*, 2530.

In-situ and micro-destructive investigation for the analysis of degradation products present on marble surfaces

Paola Fermo[a], Mario Colella[b,c], Marco Malagodi[d,e], Giacomo Fiocco[d,f], Michela Albano[d,g], Silvia Marchioron[c], Vittoria Guglielmi[a], Valeria Comite[a].

[a] Dipartimento di Chimica, Università degli Studi di Milano; [b]Dipartimento di Beni Culturali, Università degli Studi di Milano; [c]Centro studio e conservazione opere d'arte Piccolo chiostro s.r.l., Milano; [d]Arvedi Laboratory of non-Invasive Diagnostics, CISRiC, University Cremona; [e]Department of Musicology and Cultural Heritage, University of Pavia, Cremona; [f] Department of Chemistry, Università di Torino, Torino, Italy; [g]Department of Physics, Polytechnic of Milan.

Non-invasive in-situ analyses and micro-destructive investigation can be applied successfully for the analysis of degradation layers present on the marble surfaces of works of art stored both outdoor and in museum environments. The formation of these layers is mainly due to the interaction with atmospheric pollutants that react with the carbonatic substrate. The chemical and morphological characteristics of the degradation products, which highly depend on the exposure conditions, may be analyzed by means of a multi-analytical approach, including techniques such as XRF, colorimetry, FTIR-ATR and SEM-EDS, which are commonly applied to investigate works of art surfaces [1]. Furthermore, micro-destructive methodologies specifically set-up [2] allow the quantification of the carbonaceous fraction which is responsible for the dark black colour typical of outdoor crusts (fig. 1a). The analytical approach proposed was applied to the analysis of degradation products collected from outdoor statues stored at the Monumental Cemetery of Milan and from a Renaissance marble sculptural group representing a Piety (fig.1b). The results highlighted the presence of degradation layers composed by gypsum where carbonaceous particles are embedded. In the case of the Piety, after the removal of an external treatment applied for conservation purpose during the 19th century, some colour traces were highlighted. Finally colorimetric analysis turned out to be a powerful tool to verify the homogeneity of the cleaning procedure performed on the surface statue by the restorers.

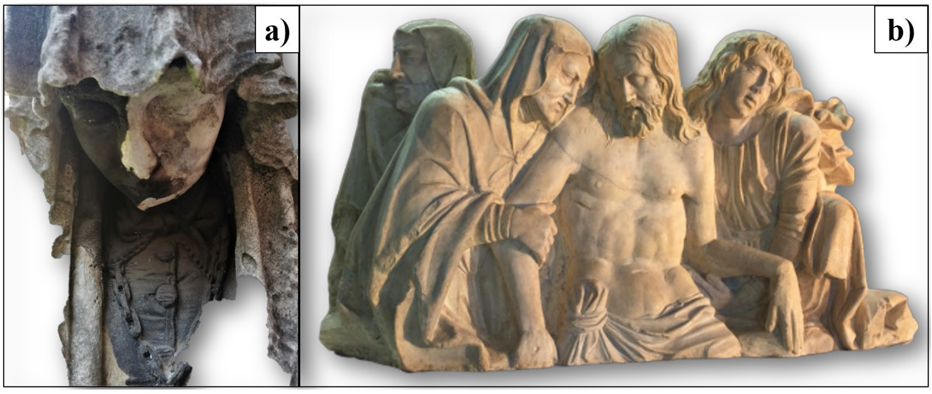


Fig .1 (a) A statue form the Monumental Cemetery of Milan with the presence of black crusts; (b) the Piety sculptural group by Gasparo Cairano, stored at the Castello Sforzesco-Museum of Ancient Art (Milan, Italy)

[1] Guglielmi, V., Andreoli, M., Comite, V., Baroni, A. and Fermo, P. The combined use of SEM-EDX, Raman, ATR-FTIR and visible reflectance techniques for the characterisation of Roman wall painting pigments from Monte d'Oro area (Rome): an insight into red, yellow and pink shades. Environmental Science and Pollution Research, 2021 https://doi.org/10.1007/s11356-021-15085-w

[2] Comite, V., Alessandro Miani, A., Ricca, M., La Russa, M., Pulimeno, M., Fermo, P. The impact of atmospheric pollution on outdoor cultural heritage: an analytic methodology for the characterization of the carbonaceous fraction in black crusts present on stone surfaces. Environmental Research, DOI: 10.1016/j.envres.2021.111565, 2021

Rotating Magnetic Chromatography, a new technique for micro-particle and cell separation

Jishou Piao[a], *Long Cai*[a], *Hyok Chol Ri*[b], *Lu Liu*[a], *Huaze Sun*[a], *Xiangfan Piao*[c], *Haibo Shang*[a], *Xuejun Jin*[b], *Qiaosheng Pu*[d], *Yong Cai*[e], *Zhongping Yao*[f], *Donatella Nardiello*[g], *Maurizio Quinto*[a,g], *Donghao Li*[a]

[a]*Department of Chemistry, Yanbian University, Park Road 977, Yanji City, Jilin Province, China 133002,* [b]*College of Pharmacy, Yanbian University, Park Road 977, Yanji City, Jilin Province, China 133002,* [c]*Engineering College Department of Electronics, Yanbian University, Park Road 977, Yanji City, Jilin Province, China 133002,* [d]*State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China,* [e] *College of Life Science, Jilin University, Changchun City, Jilin province, China 130012,* [f]*State Key Laboratory of Chirosciences, Food Safety and Technology Research Centre and Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, China,* [g]*DAFNE - Department of Agriculture, Food, Natural resources and Engineering, University of Foggia, Via Napoli 25, I-71122 Foggia, Italy*

In the last years, new chromatography techniques have appeared in the analytical chemistry panorama. Forces and interactions never used before have been exploited favorably to separate different objects, from small molecules to microparticles. In particular, microparticle separation is becoming increasingly important to study and analyze rare target cells, such as circulating tumor cells, cancer stem cells, and immune cells [1-3]. Anyway, the microparticle separation technologies applied to the analysis of disease-associated cells are still facing the problem of a loss of information on individual specific cells, caused by an ineffective separation accuracy. In this work, we have focused our interest on the development of new technologies aimed at microparticle separation, selection, and isolation. To hit this target, our research group in collaboration with different Chinese University Departments located at Yanji, Lanzhou, Changchun, and Kowloon, developed a brand-new idea, exploiting collisions between magnetic nanoparticles, forced to follow well-defined trajectories by an external magnetic field, and microparticles (like cells) flowing in a microchannel, to separate them in the function of their dimensions, with high accuracy and reproducibility. Preliminary experiments were carried out to optimize the method using fluorescein isothiocyanate-modified polystyrene particles (chosen as a reference standard). Then, the method was applied to the analysis of cancer cells like HeLa, SK-Hep-1, and Hep-3B, allowing their fast and high-resolution chromatographic separation (R = 1,0 for cells with diameters difference of 0,05 μm). Due to its unmatched sub-micrometer cell separation capabilities, RMC can be considered a breaking-through technique that can unlock new perspectives and therapies in the field of medical oncology.

[1]. D. Gao, F. Jin, M. Zhou, Y. Jiang, *Analyst* **2019**, *144*, 766.
[2]. J. L. Spudich, D.E. Koshland, *Nature* **1976**, *262*, 467.
[3]. S. J. Altschuler, L.F. Wu, *Cell* **2010**, *141*, 559.

Role of mobile phase composition in enantioselective liquid chromatography

Roccaldo Sardella, Ina Varfaj, Federica Ianni, Andrea Carotti

University of Perugia, Department of Pharmaceutical Sciences, Perugia, Italy

At the development stage of an enantioselective liquid chromatography method, the majority of R&D laboratories in private Companies prefers to rely upon column screening procedures over the optimization of the eluent composition with a few or even a single “chiral column”. Generally, screening 5-to-9 columns with a unique mobile phase is deemed to be sufficient for a correct selection of the best chiral stationary phase (CSP) for the analyte if interest. Instead, a more challenging way to obtain enantioseparations is typically faced in Academia, where the best combination of mobile phase variables able to improve the degree of complementary interactions between functional groups decorating the chiral selector (SO) of a single CSP and analyte (SA) structure, is investigated.

The SO-SA interaction mechanism is still simplistically viewed in a bimolecular way, thereby neglecting the important role of the mobile phase components in the overall enantiodiscrimination event. Indeed, eluent must not be regarded as a passive transporter of the analytes along the column, whilst it is an essential component involved in the enantioselective SO-SA association mechanism at multiple levels. Indeed, the nature of the mobile phase (i) governs the degree of SO and SA solvation, (ii) dictates their conformational preferences, (iii) influences their ionization status (for charged species) and, (iv) defines the degree of complementary intermolecular interactions between their functional groups.

In this framework, this lecture intends to present barely considered aspects concerning the impact of the eluent composition on the overall enantiorecognition process. Studies dealing with the employment of CSPs incorporating SOs based on *Cinchona* alkaloids [1], amino acids [2], crown-ethers, polysaccharides [3], glycopeptides [4] and human serum albumin will be illustrated.

[1] F. Ianni, R. Sardella, A. Carotti, B. Natalini, W. Lindner, M. Lämmerhofer *Chirality* **2016**, *28*, 5-16.

[2] R. Sardella, A. Macchiarulo, A. Carotti, F. Ianni, M.E. García Rubiño, B. Natalini, *J. Chromatogr. A* **2012**, *1269*, 316-324.

[3] R. Sardella, F. Ianni, A. Lisanti, M. Marinozzi, S. Scorzoni, B. Natalini, *Biomed. Chromatogr.* **2014**, *28*, 159-167.

[4] R. Sardella, F. Ianni, A. Lisanti, S. Scorzoni, F. Marini, S. Sternativo, B. Natalini, *Amino Acids* **2014**, *46*, 1235-1242.

The progress in peptidomics: new strategies for purification and untargeted identification of short peptides

.

Anna Laura Capriotti

Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy

Short peptide sequences (2-4 amino acids) represent emerging analytes in various fields, including biomarker discovery and food analysis, and a well-known analytical challenge in complex matrices due to the lack of dedicated analytical workflows.

Direct analysis of short peptides in complex biological matrices is not usually feasible due to the potential association with high abundant components, such as proteins, and due to the low abundance of peptides compared to other molecules, which can cause extensive ion suppression during electrospray ionization (ESI). Some of these issues can be overcome by a dedicated protocol for enrichment and clean-up of short peptides. However, sample clean-up is not straightforward either due to the heterogeneous nature of short peptides in polarity, which hinders their pre-concentration from complex matrices and their chromatographic separation. In the latter regard, the commonly used reversed-phase chromatography on C18 can efficiently separate only short peptides made up of hydrophobic residues. Alternative separation strategies have been considered to improve the coverage of short polar peptides, such as hydrophilic interaction chromatography, polar C18 , or porous graphitic carbon has been investigated to find a compromise suitable to cover a broader range of analyte polarity. Other issues in short peptide analysis include the lack of automated systems for sequence identification from high-resolution mass spectra and tandem mass spectra (MS/MS). Indeed, ordinary bioinformatics software developed for proteomics cannot identify sequences shorter than five amino acids, and metabolomics databases are currently not sufficiently complete to cover the 168,400 possible combinations of proteinogenic amino acids in dipeptides, tripeptides, and tetrapeptides, let alone possible modifications or isomeric structures [1].

This lecture aims to provide an overview of analytical solutions developed for enrichment, separation, and untargeted identification of natural and modified short peptides in biological matrices, such as urine and serum samples and food matrices (milk, fish, hemp seed, and soybean).

In particular, the use of carbonaceous material for the enrichment and separation will be discussed, highlighting the advantages of retaining polar, non-polar, acidic, and positively zwitterionic charged compounds due to strong hydrophobic and ion-exchange interaction.

Another aspect that will be discussed in detail will be developing a database implemented in Compound Discoverer 3.0, a software dedicated to the analysis of short molecules, for the creation of a data processing workflow specifically dedicated to short peptide tentative identification.

Finally, an untargeted metabolomics approach of prostate cancer zwitterionic and positively charged compounds in urine will be presented [2].

[1] S. Piovesana, A.L. Capriotti, et al. Anal Chem 2019, 45, 11474–11481
[2] Cerrato A., Bedia C, et al. ACA 2021, 1158, 338381

Analytical Challenges in the Fight Against Biological Threats. The case of Nanoantimicrobials Inhibiting the Persistency of SARS-CoV-2

Maria C. Sportelli[a], M. Izzi[a], A. Sallustio[b], Daniela Loconsole[b], Rosaria A. Picca[a], M. Chironna[b], N. Cioffi[a*]

[a] *Chemistry Department and Bari Unit of CSGI consortium, University of Bari "Aldo Moro", V. Orabona, 4, 70126, Bari, Italy.;*

[b] *Department of Biomedical Sciences and Human Oncology-Hygiene Section, University of Bari "Aldo Moro", Piazza Giulio Cesare, 1,1 70124, Bari, Italy.*

The development of nanoantimicrobials (NAMs) has been the focus of our research since early 2000s [1]. The combination of solution-based syntheses and physical deposition approaches offered a number of technological solutions for the production of active nanoparticles (NPs) and composite materials to fight antimicrobial resistance [2]. A thorough analytical characterization of the NAMs demonstrated that these nanocomposites exert a controlled release of bioactive ions (e.g. Ag^+, Cu^{2+}, Zn^{2+}) without releasing intact NPs of potential toxicity. We recently focused on water-based and scalable electrochemical routes to ZnO NPs [3] with enhanced activity towards different pathogens.

Since 2019, the new coronavirus disease (COVID-19), related to the severe acute respiratory syndrome coronavirus (SARS-CoV-2) was reported in China, and suddenly extended to Europe and America, giving rise to the pandemic we are still facing [4]. Since then, many strategies for the prevention and control of COVID-19 have been investigated. Besides pharmacological treatments and vaccines, prevention of the virus spread can help the fight against SARS-CoV-2. As to the latter aspect, one of the characteristics sought in a (nano)antiviral treatment is to ensure the cleaning and sterilization of common touch, inanimate surfaces, especially in all those contexts where contagion could run fast: hospitals and clinical laboratories, schools, transport and public places in general [5]. Another level of action could be the treatment of hospital waste and infected sludges [6].

Here we report on the efficacy of the electrosynthesized ZnO NPs against SARS-CoV-2. This topic rises interesting challenges for the Analytical Chemistry community, both in terms of active materials characterization and of the analysis of the final industrial goods, even after usage.

The results of microscopy (TEM), diffraction (SAED) and spectroscopy (UV-Vis, ATR-IR, XPS) analyses will be discussed, offering a clear view of the materials structure, chemical composition and surface reactivity. The NP antiviral activity has been tested in vitro against SARS-CoV-2, showing a decrease of the viral loading comprised between 60% and 100%, as a function of the material's composition. Application of these nanoantimicrobials as coatings for hard touching surfaces and waste disinfection is envisaged.

References:
[1] N. Cioffi, et al., *Chem. Mater.* **2005**, 17, 5255.
[2] N. Cioffi, M. Rai Eds., "Nano-antimicrobials. Progress and Prospects", Springer-Verlag Publisher, 1st Edition, ISBN 978-3-642-24427-8, 2012.
[3] R. A. Picca, et al., *Electrochim. Acta* **2015**, 178, 45.
[4] Q. Li, et al., *N. Engl. J. Med.* **2020**, 382, 1199.
[5] M.C. Sportelli, et al., *Nanomaterials*. **2020**, 10, 802.
[6] J. Lv, et al., *Environmental Science and Pollution Research*, **2021**, https://doi.org/10.1007/s11356-021-13247-4

The value of multidimensional chromatography coupled to mass spectrometry for the non-targeted metabolite profiling of natural products

Flavio A. Franchina[a,b], Lena M. Dubois[b], Martina Catani[a],
Luisa Pasti[a], Jean-François Focant[b], Alberto Cavazzini[a]

[a] University of Ferrara, Dept. of Chemistry, Pharmaceutical and Agricultural Sciences, via L. Borsari 46, 44121 Ferrara, Italy; [b] University of Liège, Dept. of Chemistry, 11 Allée du Six Août, 4000 Liège, Belgium

The use of high-resolution separation techniques in combination with the identification power of mass spectrometry is certainly among the most powerful tools for exploratory and non-targeted chemical analysis. Yet, these are ideally initiated and completed by a robust and reliable sample preparation and data analysis to obtain and extract the key information from the dense raw data set. In such a context and seen the recent trend towards the commercialization of legal cannabis in several countries [1-2], the present contribution will show a practical example on the importance of the profiling of endogenous secondary metabolites, the determination of exogenous contaminants, and the great support that a non-targeted analytical workflow can provide in doing so [3].

The analytical method involves a sorption-based extraction followed by comprehensive two-dimensional gas chromatography coupled to (high and low resolution) mass spectrometry, i.e., a GC×GC-ToF MS system. The extraction method was optimized to have optimal recovery for the chemical classes of interest. A factorial design of experiments was used to determine the most advantageous combination of the extraction conditions (solvent type, salt addition, extraction time and temperature).

The overall method was validated on a variety of recreational cannabis flowers and cannabis oil samples. It will be demonstrated that the method allowed to efficiently highlight the difference between the various cannabis strains based on the multi-chemical class information provided.

[1] Citti, C.; Russo, F.; Sgrò, S.; Gallo, A.; Zanotto, A.; Forni, F.; Vandelli, M.A.; Laganà, A.; Montone, C.M.; Gigli, G.; Cannazza, G. *Anal Bioanal Chem* **2020**, *412*, 4009-4022.

[2] Micalizzi G.; Vento F.; Alibrando, F.; Donnarumma, D.; Dugo, P.; Mondello, L. *J Chromatogr A* **2021**, 1637:461864.

[3] Franchina, F.A.; Dubois, L.M.; Focant, J-F., *Anal Chem* **2020**, 92, 10512-10520.

Removal of environmentally relevant cations: polymer inclusion membranes (PIMs)

C. Bretti[a], *P. Cardiano*[a], *C. De Stefano*[a], *R. Di Pietro*[a], *G. Lando*[a]
[a] *Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali CHIBIOFARAM, Università degli Studi di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina*

Despite heavy metals are generally present in the environment at very low concentrations, they can generate a wide range of negative effects on the environment and on humans. The impact of pollutant metal cations on the environment is related to their marked tendency to accumulate in animal and plant tissues. These inorganic pollutants are present in all environmental compartments since they reach waters, soils and atmosphere by improper industrial waste disposal. Considerable efforts have been devoted to develope suitable methods and materials to recovery these metals, or pollutants in general. In this scenario, PIMs (i.e. Polymers Inclusion Membranes [1]) have been developed and tested for remediation purposes. PIMs, a type of liquid membranes in which the liquid phase is held within the polymeric network of a base-polymer, are used mainly for the separation of heavy and toxic metals from aqueous solutions [2]. The research on PIMs has increased exponentially over the past decade and their applications have spread in all sectors of analytical chemistry. For instance, PIMs are used as the extraction, preconcentration and phase transfer medium for numerous cations and anions. In chemical sensing, PIMs have found important uses as the active sensing membranes in electrochemical (ISE) [3] and optical sensors (Optodes and Paper-Based Devices). In addition, PIMs have been adapted for use in on-line flow analysis systems and as the accumulation medium in passive samplers for monitoring environmental pollutants. From literature data it has been observed that some PIM compositions provide much higher transport rates of metal than their SLM (supported liquid membrane) counterparts, but reasons remain unclear. To better understand this phenomenon, some researchers have investigated the structure of PIMs with a view to obtaining information regarding the way carrier and other membrane components interact and the mechanism for mass transport within the membrane. In this talk the various components used for the PIMs production will be discussed, together with the results obtained in metal cations sequestration attempts and briefly the possibility to modify PIMs by using sustainable polymeric matrix adding selected eco-friendly extractants which are expected to interact with metals in the membrane bulk or onto its surface. The challenge for the future is the research on new carriers and/or plasticizers to reduce the costs for the synthesis of PIMs on an industrial scale, and obviously, further investigations still need to be carried out to understand the relationships among the factors (membrane composition, nature of feed phase, properties of extractant, pH, temperature, etc.) affecting the transport mechanism in PIM.

[1] Y.Y.N. Bonggotgetsakul, M. Ashokkumar, R.W. Cattrall, S.D. Kolev. *J. Membr. Sci.* (2010) 365 (1-2), 242-247.

[2] C.V.I Gherasim, G. Bourceanu, R.I. Olariu, C. Arsene. *J. Memb. Sci.*(2011), 377, 167-174.

[3] E. Bakker. *Trac Trends in Analytical Chemistry* (2014), 53, 98-105

A New Strategy for Overcoming the Volcano in Water Photosplitting: Controlled Periodic Illumination

F. Pellegrino,[ab] F. Sordello,[a] M. Prozzi,[a] C. Minero,[a] V. Maurino[ab]

[a] *Dipartimento di Chimica and NIS Center, University of Torino, Via P. Giuria 7, 10125 Torino, Italy.;*
[b] *JointLAB UniTo-ITT Automotive, Via Quarello 15/A, 10135 Torino, Italy*

In the next decades, the conversion of solar energy into electricity and solar fuels will be of crucial importance for a green and sustainable future. [1] The economic recovery after the pandemic will necessarily have to start by changing old paradigms with an energy transition towards renewable and clean sources. Italy has developed its own recovery plan (PNRR) in which 23.78 billion euros will be invested for the energy transition, of which 3.19 will be used to promote the production, distribution and use of hydrogen. [2] However, many challenges remain to produce and exploit it in an efficient way, in particular green hydrogen. [3]

In this context, water splitting using semiconductor photo-catalysts has been considered a sustainable method to produce clean hydrogen (H_2) fuel. [4] Nevertheless, H_2 photo-production efficiency remains still low, although extensive research effort has been carried out in these years about the mechanisms of the Hydrogen Evolution Reaction (HER) and the Oxygen Evolution Reaction (OER). [5] In this respect, TiO_2 is a key photoactive material, usually employed with a co-catalyst deposited onto the surface to enhance charge carriers' separation and catalyze surface charge transfer reactions. [6] Even with a noble metal catalyst, the hydrogen evolution reaction can be limited by the strong M-H bonding over some metals, such as Pt, Pd and Rh, inhibiting hydrogen desorption. H absorption is regulated by the potential at the metal nanoparticles. A possible strategy to enhance the hydrogen production could be the use of a Controlled Periodic Illumination (CPI). [8] Moreover, CPI can be a valuable tool to study HER mechanism. Assuming a fast variation of the photo-potential due to the alternation of light and dark periods, it is possible to favor the H_2 desorption from the metal surface. In this way it is possible to "climb" the Trasatti's volcano plot, increasing the efficiency of those catalysts that present a limitation in the desorption step. The hydrogen evolution rate and mechanism under CPI was studied with a combination of electrochemical, spectroscopic and chromatographic methods. CPI increased H_2 production rate in the presence of Pt, Rh and Pd, whereas with Au and Cu no effect was observed. [9] These findings could also be useful for developing new sensor concepts.

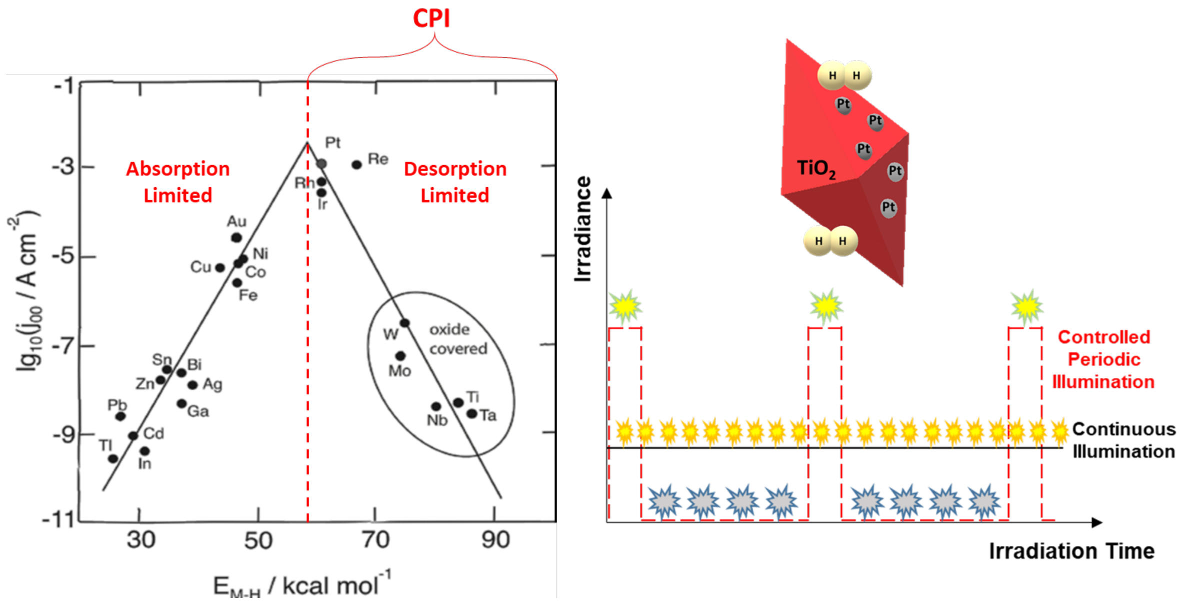


Figure 1. Trasatti's Volcano Plot for the HER in acid solutions (graph from [7]) and schematic representation of Pt deposited nanoparticles on TiO_2 and CPI concept.

[1] A. Hauch et al., Recent advances in solid oxide cell technology for electrolysis. Science 370, (2020).
[2] https://www.governo.it/sites/governo.it/files/PNRR.pdf
[3] Z. W. Seh et al., Combining theory and experiment in electrocatalysis: Insights into materials design. Science 355, (2017).
[4] S. U. Khan et al., Efficient photochemical water splitting by a chemically modified n-TiO_2. Science 297, 2243-2245 (2002).
[5] N. Armaroli, V. Balzani, The hydrogen issue. ChemSusChem 4, 21-36 (2011).
[6] F. Pellegrino et al.; ACS Catal. 2019, 9, 8, 6692–6697
[7] P. Quaino et al. Beilstein J. Nanotechnol. 2014, 5, 846–854.
[8] M. Prozzi et. al.; ACS Catal. 2020, 10, 16, 9612–9623
[9] F. Sordello et al.; ACS Catal. 2021, 11, 11, 6484–6488

Variable selection with a focus on multi-way and multi-block data

Alessandra Biancolillo[a]

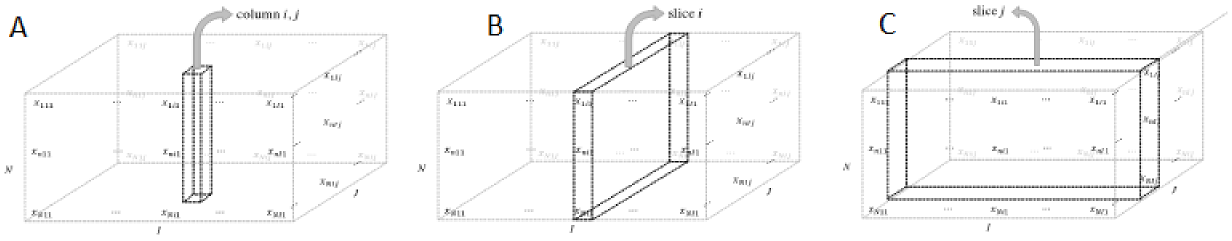
[a] *University of L'Aquila, Via Vetoio, 67100, Coppito, L'Aquila, Italy*

In data analysis, how to select meaningful variables is a hot and wide-debated topic and several variable selection (or *feature reduction*) approaches have been proposed into the literature. These methods aim at different purposes; they can be used to reduce the number of total variables and restrict it to the most significant ones for the problem under consideration, or simply for interpretative purposes, in order to understand which features contribute the most to the investigated system.

In general, variable selection strategies are divided into three main categories: *filter*, *wrapper* and *embedded* methods. In addition to these three classes, a further meta-category, presenting intermediate characteristics between filter and embedded approaches, can be identified. In fact, some feature selection approaches, like Covariance Selection (CovSel) [1], provide a filter selection based on model parameters embedded in the model building. CovSel is conceived to select variables in regression and discrimination contexts, and it assesses the features' relevancy based on their covariance with the response(s). Although variable selection methods are numerous and they have been quite widely debated into the literature, most of them refer to contexts in which data are collected in matrices, and not in more complex structures, like multi-way or multi-block data sets, where it would have even a greater reason to be applied.

This aspect is not due to irrelevance of the topic; on the contrary, the possibility of selecting information in such complex data sets is crucial.

Concerning feature selection in high-order structures, Cocchi and collaborators developed a variable selection approach for this kind of data, extending the application of VIP analysis to high multi-dimensional arrays. A further solution is represented by N-CovSel, the extension of CovSel to multi-way structures. Nevertheless, due to the multidimensional nature of data, how to select features is not trivial, and more than one solution is possible (Figure 1). This, from one side, could be seen as a drawback, but, on the other, opens up to different solutions tailored to the final purpose of the analysis. In a multi-block context, how to proceed is not straightforward as well. In fact, it has been shown that different solutions may be preferable, depending on the way the information between the different sources of variability is extracted, and according to the nature of the available data. In this context, sequential methods can give a further twist, conferred by the fact that, by construction, they allow the removal of redundant information between the data blocks.



[1] J. M. Roger, B. Palagos, D. Bertrand, E. Fernandez-Ahumada, *Chemom. Intell. Lab. Syst.* **2011**, *106*, 216.

[2] S. Favilla, C. Durante, M. L. Vigni, M. Cocchi, *Chemom. Intell. Lab. Syst.* **2013**, *129*, 76.

Near infrared hyperspectral imaging combined with multivariate image analysis: potential and limitations for the identification of microplastics in aquatic samples

Cristina Malegori [a], *Stefania Piarulli* [b,c], *Ferrante Grasselli* [b], *Laura Airoldi* [b,d], *Silvia Prati* [e], *Rocco Mazzeo* [e], *Giorgia Sciutto* [e], *Paolo Oliveri* [a]

[a] *DIFAR - Department of Pharmacy, University of Genova, Viale Cembrano 4, 16148 - Genova*
[b] *UO CoNISMa - Department of Biological, Geological and Environmental Sciences and Interdepartmental Research Centre for Environmental Sciences, University of Bologna, Via S. Alberto 163, 48123 - Ravenna*
[c] *SINTEF Ocean - Department of Clima and Environment, Brattørkaia 17 C, 7010 - Trondheim, Norway*
[d] *Department of Biology, Chioggia Hydrobiological Station Umberto D'Ancona, University of Padova, 30015 - Chioggia*
[e] *Department of Chemistry "G. Ciamician", University of Bologna, Via Guaccimanni 42, 48121 - Ravenna*

Analytical chemists are, nowadays, increasingly requested to develop reliable instrumental methods that enable the study of heterogeneous samples in a direct and non-destructive way. In this context, hyperspectral imaging in the near infrared region (HSI-NIR) provides a reliable answer, especially if coupled with innovative approaches of data processing, which combine chemometrics and image analysis. Thanks to the development of dedicated analytical strategies, it is possible to extract useful information from the so-called hypercubes (3D data arrays) of HSI-NIR, with the aim of performing multivariate pattern recognition, both exploratory and supervised, leading to efficiently characterise and monitor samples according to NIR absorption bands.

Microplastics (MP) constitute one of the most critical environmental challenges of the last decade, with potential consequences on the ecosystems and human health, and their identification in aquatic samples is a prominent case-study for exploiting all the advantages of HSI-NIR and multivariate image analysis. Aquatic organisms, in fact, are demonstrated to be the final recipient for MP contamination and, moreover, the smaller the MP size, the higher the environmental risk, as well as the analytical difficulties in detecting and characterising the particles.

In light of these considerations, the present work proposes NIR-HSI (working in the spectral range 1000-2500 nm) as an analytical method for the identification and characterisation of small MP, down to 50 μm, in aquatic samples. Given that this technique does not require extensive sample manipulation, MP are directly investigated on the filters used for the aquatic samples as a separation step, with no pre-sorting (as requested in other spectroscopic techniques such as FT-MIR microscopy). For testing the proposed strategy, samples prepared by filtration of both digested soft tissue of individual mussels, and sea water samples, artificially contaminated with different MP (polypropylene, polystyrene and polyamide) were analysed.

Chemical maps of the filters were obtained by calculating normalised difference images (NDIs), a data processing strategy able to enhance spectral differences between the cellulose background of the filter and the MP polymer. Evaluation of NDIs in combination with the spectral profile of selected pixels allowed the analyst to differentiate between the three MP polymers investigated, providing information useful for understanding the origin of the plastic contamination.

The outcomes of the present study confirmed that HSI-NIR is a reliable analytical tool for investigating heterogeneous samples and, thanks to its advantages, it is potentially automatable in large scale implementations.

Acknowledgment: financial support by Università degli Studi di Genova (Research Project *Curiosity Driven 2020*: "3Depth – From 2D to 3D hyperspectral imaging exploiting the penetration depth of near-infrared radiation", CUP: D34G20000100005) is gratefully acknowledged.

Unconventional Electrochemical Approaches for the Direct Readout of Chiral Information

Serena Arnaboldi,[a,b] Gerardo Salinas,[a] Nicolas Mano,[c] Tiziana Benincori,[d] Roberto Cirilli,[e] Alexander Kuhn[a]

[a] *Univ. Bordeaux, CNRS UMR 5255, Bordeaux INP, ENSCBP, 16 avenue Pey Berland, 33607 Pessac, France, serena.arnaboldi@unimi.it*
[b] *Univ. degli Studi di Milano, Dip. di Chimica, Via Golgi 19, 20133 Milano, Italy*
[c] *Centre de Recherche Paul Pascal, CNRS UMR5031, Univ. Bordeaux, Avenue Albert Schweitzer, 33600 Pessac, France*
[d] *Univ.degli Studi dell'Insubria, Dip. di Scienza e Alta Tecnologia, Via Valleggio 11, 22100 Como, Italy*
[e] *Centro Nazionale per il Controllo e la Valutazione dei Farmaci, Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Roma, Italy*

Among the different strategies to endow conducting polymers with chiral features, the concept of inherent chirality is extremely attractive and efficient for several reasons. [1] Inherent chirality is an intrinsic propriety of the whole molecule in which the stereogenic element responsible for chirality coincides with the functional group responsible for the specific properties of the molecular material. The racemization barrier of these molecules is high enough to allow the separation into stable enantiomers by chiral HPLC. Their electro-oligomerization results in chiral electrode surfaces able to discriminate the antipodes of chiral species by differences in peak potential recorded by voltammetry. [2] This is a true advantage from an analytical point of view, because it is possible to achieve the enantioselective discrimination in racemic mixtures of the analyte, in contrast to most of the approaches presented in literature for which the recognition is only based on differences in current intensity. In this context the high enantioselectivity of such chiral surfaces was used to develop *i)* a new approach based on bipolar electrochemistry for the absolute on-off recognition of enantiomers of a chiral probe, [3] and *ii)* new autonomous enzymes based swimmers able to convert chiral information present at the molecular level into macroscopic enantioselective trajectories. [4]

[1] Arnaboldi, S.; Magni, M.; Mussini, P. R. *Curr. Opin. Electrochem.* **2018**, 8, 60−72.
[2] Arnaboldi, S.; Benincori, T.; Cirilli, R.; Kutner, W.; Magni, M.; Mussini, P. R.; Noworyta, K.; Sannicolò, F. *Chem. Sci.* **2015**, 6, 1706− 1711.
[3] Arnaboldi, S.; Gupta, B.; Benincori, T.; Bonetti, G.; Cirilli, R.; Kuhn, A. *Anal. Chem.* **2020**, 92, 10042−10047.
[4] Arnaboldi, S.; Salinas, G.; Karajic, A.; Garrigue, P.; Benincori, T.; Cirilli, R.; Bichon, S.; Gounel, S.; Mano, N.; Kuhn, A. *Nat. Chem.* **2021**, *in press*

Electrosynthesis of Layered Double Hydroxides for analytical applications

Isacco Gualandi[a], *Elisa Musella*[a], *Erika Scavetta*[a], *Domenica Tonelli*[a]

[a] *Dipartimento di Chimica Industriale 'Toso Montanari', Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy (isacco.gualandi2@unibo.it)*

Layered double hydroxides (LDHs) are anionic clays which offer fascinating proprieties in the development of electrochemical sensors. Chemical tunability, ion exchange capability and low cost play a key role in the successful applications of this class of materials. Tonelli's group proposed a quick electrosynthesis procedure which has been exploited for the fabrication of LDH chemically modified electrodes usable in a large plethora of electrochemical devices [1]. The firstly-developed potentiostatic procedure was based on a cathodic potential pulse to generate a local pH increase that led to the formation of a thin LDH film on a conductive substrate. Sensing applications take advantage of LDHs with metal ions (Ni^{2+} and Co^{2+}) that can undergo reversible redox reactions to confer electrical conductivity to the clay and mediate the electron transfer between the analyte and the electrode surface [2]. The electrocatalytic behavior underpins the development of sensors for the detection of alcohols, sugars, amines and phenols and the electrosynthesis optimization allows to tune the LDH films to enhance their performance in different analytical applications. Moreover, enzymes (Glucose oxidase and Lactate oxidase) can be entrapped in the LDH structure during electrosynthesis to produce conventional amperometric devices and/or organic electrochemical transistors for the detection of glucose and lactate [3].

However, the potentiostatic approach does not permit the variation of the LDHs composition with good reproducibility, so hindering the benefit stemmed from their chemical tunability. A novel potentiodynamic protocol has been developed for the synthesis of LDHs with precise Me(II)/Me(III) ratios, as such or intercalated with carbon nanomaterials. The films have been thoroughly characterized by electrochemical and spectroscopic methods, and electron microscopy. The electrocatalytic features have been investigated for Co(II) and Ni(II) based LDHs. As to the former cation, the effect of Me(II)/Me(III) ratio on oxygen evolution reaction was investigated [4], while the electrocatalytic oxidation was proposed as transduction principle for sensing of 5-(hydroxymethyl)furfural [5]. The combinations of Ni based LDHs with carbon nanomaterials produce [6] composites that exhibit a large active area, and a boosted charge transfer between the active Ni^{2+} centers and electrode surface. The composites allow for the fabrication of glucose sensors with high sensitivity ($2.6\ A\ M^{-1}\ cm^{-2}$) and low limit of detection (0.6 μM) [6].

[1] E. Scavetta, B. Ballarin, M. Giorgetti, I. Carpani, F. Cogo, D. Tonelli, *J. New Mater. Electrochem. Syst.* **2004**, *7*, 43–50.

[2] D. Tonelli, I. Gualandi, E. Musella, E. Scavetta, *Nanomaterials* **2021**, *11*, 725

[3] I. Gualandi, M. Tessarolo, F. Mariani, D. Arcangeli, L. Possanzini, D. Tonelli, B. Fraboni, E. Scavetta, *Sensors*, **2020**, *20*, 3453

[4] E. Musella, I. Gualandi, E. Scavetta, M. Gazzano, A. Rivalta, E. Venuti, M. Christian, V. Morandi, D. Tonelli, *Chem. Eur.J.* **2019**, *25*,16301.

[5] E. Musella, I. Gualandi, E. Scavetta, A. Rivalta, E. Venuti, M. Christian, V. Morandi, A. Mullaliu, M. Giorgetti, D. Tonelli, *J. Mater. Chem. A* **2019**, *7*, 11241.

[6] I. Gualandi, Y. Vlamidis, L. Mazzei, E. Musella, M. Giorgetti, M. Christian, V. Morandi, E. Scavetta, D. Tonelli, *ACS Appl. Nano Mater.* **2019**, *2*, 143.

AllerT: a Matlab-based workflow for putative allergens identification in novel foods via LC-ESI-MS/MS analysis

G. Ventura[a], *M. Bianco*[a], *C.D. Calvano*[b,c], *I. Losito*[a,b], *T.R.I Cataldi*[a,b]

[a]*Department of Chemistry,* [b]*Interdepartmental Research Center SMART* [c]*Department of Pharmacy-Pharmaceutical Sciences, University of Bari Aldo Moro, via Orabona 4, 70126, Bari, Italy*

The incidence of food allergy has increased in latest years and is now recognized as an important public health problem [1]. Subsets of proteins of the most common allergenic foods that induce hypersensitivity reactions are well known and recognized [2]. However, since globalization, growing ethnic diversity and nutrient sources of *novel foods* come to our tables, studies on unusual food allergenic proteins are demanded [3]. For example, microalgae and cyanobacteria such as spirulina (*Arthrospira platensis*) and chlorella (*C. vulgaris*) have been recognized as emerging “superfoods” due to their proteins, lipids, and oligo-elements contents. Unfortunately, allergenic reactions including anaphylaxis due to spirulina have been described [4]. Due to many additional, not well-characterized ingredients, *in-silico* assessment of allergenicity is becoming an interesting alternative for allergen screening. Potential risks of allergic cross-reactivity can be evaluated by comparing amino acid sequences against known allergens in available databases, such as AllergenOnline (www.allergenonline.org), which allows the recognition of putative allergens through an overlapping between the amino acid sequences of the protein under examination and all the allergenic protein sequences present in the database, depending on established parameters [5]. However, the procedure is time-consuming and cannot be automatized for high-throughput analysis. Several allergen databases amenable to facilitate high throughput 'post data acquisition allergen analysis' are described in the literature. However, these pipelines need to be automated and compared, since different results can be obtained.

In this communication a Matlab-based workflow, which addresses some main issues pertinent to potential *Aller*gens iden*T*ification (*AllerT*) in terms of univocal and harmonic output, will be illustrated and discussed. Developed software can help in predicting the hypothetical allergenicity of proteins in novel foods by exploiting the sequence similarity with a data set of known allergens. The inputs are represented by protein codes obtained following a bottom-up proteomics approach; the output proteins are divided into three groups: (I) known allergens (100% identity), (II) proteins with >70% identity with listed allergens, and (III) proteins with >50% identity, chosen as the probable threshold value of cross-reactivity [6]. *AllerT* can perform *in-silico* digestions, using single or enzyme combinations of putative discovered allergenic proteins, also identifying similar or identical peptides of known allergenic proteins. Herein, AllerT is applied to some conventional and novel foods.

Acknowledgments

This work was supported by projects: (i) PONa3_00395/1 “BIOSCIENZE & SALUTE (B&H)” and (ii) Progetto di Ricerca di Interesse Nazionale-PRIN 2017YER72K- “*Development of novel DNA-based analytical platforms for the rapid, point-of-use quantification of multiple hidden allergens in food samples*”, financed by the Italian Ministero per l’Istruzione, l’Università e la Ricerca (MIUR).

References

[1] H. Renz, K.J. Allen, *Nat. Rev. Dis. Prim.* **2018**, *4*, 17098.
[2] G.A. Bannon, *Curr. Allergy Asthma Rep.* **2004**, 4, 43
[3] European Food Safety Authority, **2021***, www.efsa.europa.eu/en/topics/topic/novel-food*
[4] M. Petrus, R. Culerrier, et al., *Allergy*, **2009**, 65, 924.
[5] M. Abdelmoteleb, C. Zhang, et al., *Food Chem. Toxicol.*, **2021**, 147, 111888.
[6] R.C. Aalberse, *J. Allergy and Clin. Immun.*, 2000, 106, 228.

Enzyme based Amperometric Biosensors: From Direct Electron Transfer to Chimeric Enzymes

Paolo Bollella[a,b]

[a] Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", 70125 Bari, Italy
[b] Department of Chemistry and Biomolecular Science, Clarkson University, Potsdam, NY 13699–5810, United States

paolo.bollella@uniba.it

Current research on enzyme based amperometric biosensors deals essentially with the same target analytes as was at focus in the early days of biosensor research, that are those within the clinical/medical, food/agriculture, and environmental fields. However, there has been substantial progress through the years and progress continues [1].

Communication between a redox enzyme and an electrode has been a central theme and continues along the traditional three major electron transfer (ET) routes, that are 1st, 2nd (mediated electron transfer) and 3rd generation biosensors (direct electron transfer, DET). DET consists in the direct electronic connection between the redox center of the enzyme and the electrode surface, which is working as a signal transducer. DET has been the target for many investigations both as a scientific challenge but also for practical reasons as a DET approach would simplify the construction of a biosensor and minimize the influence of other possible interfering components in the sample as well as allow mechanistic studies of the enzyme [2].

Beyond DET, another important topic within enzyme based amperometric biosensors is the possibility to target analytes that are not involved in ET chains by using chimeric/allosteric enzymes. In the last decade, the rise of synthetic biology has driven the efforts to construct artificial allosteric protein switches in order to detect such target analytes. Typically, the construction of chimeric enzymes occurs via insertion of a regulatory receptor domain into the biocatalytic reporter domain. Construction of such chimeric enzymes utilizes the recombinant DNA technology that is a core technology of protein engineering [3].

In this regard, we have investigated the bioelectrocatalytic properties of pyrroloquinoline quinone-dependent glucose dehydrogenase fusion with calmodulin (PQQ-GDH-CaM). This protein is catalytically inactive in its ground form but can be activated by the addition of calmodulin binding peptide that induces its conformational transition and activation. This system was practically utilized to realize multipurpose biosensors platforms(e.g., glucose detection, peptide detection, rapamycin etc.) [4].

References

[1] P. Bollella, L. Gorton, *Curr. Opin. Electrochem.* **2018**, 10, 157-173.
[2] P. Bollella, E. Katz, *Sensors.* **2020**, 20, art. No. 3517.
[3] P. Bollella, et al., *J. Phys. Chem. Lett.* **2020**, 11, 5549-5554.
[4] P. Bollella, et al., *ACS Sensors,* under review .

Study and application of chemical models to measure the urine saturation with calcium salts

Silvia Berto [a], Martino Marangella [b], Concetta De Stefano [c], Demetrio Milea [c], Pier Giuseppe Daniele [a].

[a] Università di Torino, Dipartimento di Chimica, via P. Giuria 7, 10125 Torino, Italy; [b] Fondazione Scientifica Ospedale Mauriziano-Onlus, via Magellano 1, Torino, Italy, [c] Università degli Studi di Messina, Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, CHIBIOFARAM, V.le F. Stagno d'Alcontres 31, 98166 Messina, Italy.

Nephrolithiasis (NL) is a common disease and it is characterized by high rates of recurrence [1]. The metabolic and physicochemical evaluation of urine may help to guide physicians to choose adequate therapies and to control for patients' compliance [2]. The saturation state (β values) is assessed by the determination of free concentrations of kidney stone constituent ions. These values are estimated by considering the main ionic soluble complexes; the complexes formed depend on the components of urine and their concentration depends on their stability constant. The definition of a complete chemical model, in which all the species that can affect the saturation levels are taken into account, as well as to estimate dependable formation constants, are crucial to attain a reliable estimation of the risk of stones formation. Years ago, the urine chemical model was studied and the formation constants of most of the species involved in the urine saturation with calcium salts were estimated. Several computer-based calculations for evaluating urine saturation with stone-forming salts were also developed, including URSUS [3], EQUIL [4], and JESS [5]. More recently, Lithorisk® [6] substituted URSUS. The use of these programs has been proposed and recommended in the management of patients with NL [7] and the measurement of the relative supersaturation, based on a thermodynamic approach, is often included in diagnostic work-up. It is contended that this approach is liable to overestimation of β values because some complexes may be overlooked, but the updating of the chemical models continues. The aim of a recent work was to assess whether two so far neglected complexes, $[Ca(PO_4)Cit]^{4-}$ and $[Ca_2H_2(PO_4)_2]$, proposed by the recent literature, can be relevant to explain the chemistry of urine. With this aim, the Ca-phosphate-citrate aqueous system was investigated by potentiometric titrations at 37°C. The experimental data show that the $[CaPO_4]^-$ species is present in solution, whereas the formation of the ternary complex $[Ca(PO_4)Cit]^{4-}$ is quite improbable. The formation of the dimeric species was excluded, as already reported [8]. Therefore, $[CaPO_4]^-$ species may have an impact on saturation levels at higher pH and it will be included in the chemical model used by Lithorisk® software, while the formation of the ternary complex can be rejected.

[1] M.S. Pearle, E.A. Calhoun, G.C. Curhan, *J Urol.* **2005**, *173*, 848.
[2] J.C.Jr. Williams, G. Gambaro, A. Rodgers, J. Asplin, O. Bonny, A. Costa-Bauzá, P.M. Ferraro, G. Fogazzi, D.G. Fuster, D.S. Goldfarb, F. Grases, I.P. Heilberg, D. Kok, E. Letavernier, G. Lippi, M. Marangella, A. Nouvenne, M. Petrarulo, R. Siener, H.G. Tiselius, O. Traxer, A. Trinchieri, E. Croppi, W.G. Robertson, *Urolithiasis* **2021**, *49*, 1.
[3] P.G. Daniele, C. De Stefano, M. Marangella, C. Rigano, S. Sammartano, *Biochim Clin* **1989**, *13*, 507.
[4] P.G. Werness, C.M. Brown, L.H. Smith, B. Finlayson, *J Urol*. **1985**, *134*, 1242.
[5] P.M. May, K. Murray, *Talanta* **1991**, *38*, 1409.
[6] M. Marangella, M. Petrarulo, C. Vitale, P.G. Daniele, S. Sammartano, *Urolithiasis* **2021**, *49*, 211.
[7] P.M. Ferraro, A. Ticinesi, T. Meschi, A. Rodgers, F. Di Maio, P. Fulignati, L. Borghi, G. Gambaro, *J Urol*. **2018**, *200*, 1082.
[8] P.G. Daniele, C. Rigano, S. Sammartano, *Ann Chim*. **1982**, *72*, 341.

2D Nanomaterials: among functional natural compounds and affordable sensor designs

Flavio Della Pelle

Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Campus "Aurelio Saliceti" via R. Balzarini 1, 64100 Teramo, Italy.

The ongoing green transition pushes towards the use of natural compounds instead of synthesized chemicals in different scientific and industrial fields. In this framework, the use of low environmental impact materials, renewable sources, and by-products have burst also in the analytical scenario. Biological and phytochemical compunds can offer a plethora of fascinating optical, electrochemical and structural properties that pave the way toward their creative and unconventional use in (bio)sensors development.

Among phytochemicals, phenolic compounds (PCs) are demonstrating to be 'useful tools' in the nanomaterial and (bio)sensors domain, overcoming their conventional role of antioxidant and healthy compounds. PCs properly used can act as stabilizers, modifiers, bonding generators able to assist the formation and assembling of nanomaterials and their heterostructures. More captivating, the coupling of nanomaterial and PCs, can drive to functional nanomaterials with integrated analytical useful features.

In a parallel track, the fabrication of devices integrating fully nanomaterials-based conductive films is still a research hot topic, particularly for flexible devices. Despite many manufacturing strategies that have been proposed, low-cost substrates (flexible plastic, paper, etc.) and everyone's reach instruments, still representing the more captivating and sustainable route, and although much progress has been made, there are still unexplored rooms.

This presentation will be focused on our experience in using natural compounds as building blocks for the implementation of lab-made (bio)sensors based on nanomaterials. Here, an overview of a horizontal systematic study in which several natural PCs, with different structures, have been challenged as functional 'surfactants' to obtain 2D-nanosheets and natural nanofibers will be presented. Graphite, group VI transition metal dichalcogenides (i.e., MoS_2, WS_2, $MoSe_2$, and WSe_2), and biochar have been successfully exfoliated in water and their electrochemical and gas sensing ability explored, by using different sensing configurations. Moreover, this presentation will give also an overview of the use of the produced nanomaterials to construct self-supported conductive films integrated into flexible (bio)sensors, produced with affordable benchtop technologies. In particular, the fabrication of devices integrating nanomaterials using low-cost substrates (thermoplastic, polymeric sheets, and paper) and office-grade microfabrication technologies will be presented.

This presentation aims to prove how properly selected natural compunds allow producing nanomaterials with stand-out and also unexpected features, particularly prone to be integrated into affordable cutting-edge (bio)sensors and analytical devices.

Celector(R): the cell chromatography for quality control of living cells

B. Roda[a,b], S. Zia[b], V. Pizzuti[c], A. Maggio[c], F. Alviano[c], L. Bonsi[c], A. Zattoni[a,b], P. Reschiglian[a,b]

[a]Department of Chemistry "G. Ciamician", Bologna, Italy; [b]Stem Sel, Bologna, Italy; [c]Department of Experimental, Diagnostic and Specialty Medicine, Unit of Histology, Embryology and Applied Biology, University of Bologna, Bologna, Italy

Population ageing, injuries, cancer surgery: cell-based regenerative therapies are strongly expanding. We need new technologies for quality control and non-invasive isolation of cells used for therapy, for maximum safety towards new clinical applications.

The development of new methods and technologies for cell separation, sorting, selection, isolation, or enrichment are becoming a challenging task for many bioanalytical applications [1], as described below. In order to realize the concept of "precision medicine", the research aims at addressing issues for the analysis of liquid biopsy targets, such as rare cells. In the field of preclinical studies for anticancer drugs, the development of new high-tech systems for screening is one of the main problems; indeed, among studied anticancer drugs only a small percentage reach clinical approval. Due to the high cost and longtime clinical development, new, more effective preclinical drug-screening platforms represents an important challenge [2]. Stem cells therapy within the advance therapy medicinal product is increasing worldwide in particular for the treatment of osteoarticular defects, heart failure, kidney injury, diabetes and haematological disorders among many [3]. Stem cells can be found in every tissue but access is not always easy and cannot be derived in high numbers. The gold standard procedure for tissue processing is the enzymatic treatment with collagenase type II that allow the release of cells entrapped in the extracellular matrix complex. However, this procedure required lab processing, time and several additional manipulation steps that can alter cell functionality and the cells' yield; for this reason, mechanical procedure of digestion have been increasingly used. The quality of these cells depends on isolation method and culture condition and must be assessed for stability, toxicity and senescence [4].

In this paper we present a new technology, Celector®, for the quality control and sorting of living cells. Celector®, that we called cell chromatograpy, has shown able to tag-less analyze, discriminate and separate a wide size range of cells based on their physical characteristics, with high resolution and throughput and with totally maintenance of native properties [5, 6]. The separation is obtained in a short time (around 15 minutes) in a rectangular shape capillary device, where cells suspensions are eluted through a laminar flow of mobile phase. Injected cells reach a specific position across the channel thickness during transportation due to the combined action of gravity, acting perpendicularly to the flow, and opposing lift forces that depend on the morphological features of the sample. Cells at a specific position in the channel acquire well-defined velocities and are therefore eluted at specific times. A micro-camera is connected as a detector and specifically designed software was developed for image acquisition, post-processing and data analysis. The first output of the instrument is a live fractogram representing eluted cells respect time of analysis and it is the fingerprint of the biological sample. Cells with different elution time can be collected in separate fractions and used for further studies or direct applications.

Several applications show how the multipotent component from heterogeneous populations of stem cells can be selected without extra manipulation. This enriched population can be used for several applications in basic and applied research.

The results demonstrate the use of Celector® as analytical platform for the quality control of cells used for drug screening, with fundamental improvement of preclinical tests; and as an interesting technology to obtain homogeneous and "good" cell therapy products to improve the success of regenerative medicine applications.

[1] Malgorzata A.W., Ian M.F., Steven A.S. *Anal Chem.* **2020**, *92*, 105-131
[2] Kitaeva K.V., Rutland C.S., Rizvanov A., Solovyeva V. *Front. Bioeng. Biotechnol.* **2020**, doi.org/10.3389/fbioe.2020.00322
[3] Samadi P., Saki S., Khoshinani H.M., Sheykhhasan M. *Curr Stem Cell Res Ther.* **2020**, doi:10.2174/1574888X15666200914142709.
[4] Neri S. *Int J Mol Sci.* **2019**; *20(10)*, 2406
[5] Roda B, Lanzoni G, Alviano F, Zattoni A, Costa R, Di Carlo A, Marchionni C, Franchina M, Ricci F, Tazzari PL, Pagliaro P, Scalinci SZ, Bonsi L, Reschiglian P, Bagnara GP. *Stem Cell Rev Rep.* **2009**, *5(4)*, 420.
[6] Casciaro F, Zia S, Forcato M, Zavatti M, Beretti F, Bertucci E, Zattoni A, Reschiglian P, Alviano F, Bonsi L, Follo MY, Demaria M, Roda B, Maraldi T. *Cells*. **2021,** *10(1)*,158.

Mineral oil investigation in omega-3 rich lipid supplements by using multidimensional liquid-gas chromatography

Alessia Arena [a], *Mariosimone Zoccali* [b], *Peter Q. Tranchida* [a], *Luigi Mondello* [a,c,d,e]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b] *Department of Mathematical and Computer Science, Physical Sciences and Earth Sciences, University of Messina, Messina, Italy;*
[c] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[d] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[e] *Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy.*

In the past few decades, omega-3 lipid supplements have become increasingly popular with consumers, due to their multiple health benefits. The present research is focused on the evaluation of mineral oil hydrocarbon (MOH) contamination in seventeen commercial supplements with different formulations. Analysis were performed using an on-line liquid chromatography-gas chromatography-flame ionization detection (LC-GC-FID) system, nowadays considered the most efficient approach for MOH analysis in foodstuffs.

The use of an LC silica column, in the normal phase mode, allows to carry out both a sample preparation, by removing the bulk of the matrix (mainly lipids), and a pre-separation step by achieving the separation of mineral oil saturated hydrocarbons (MOSHs) from mineral oil aromatic hydrocarbons (MOAHs). The LC-GC transfer step was performed using the retention gap technique, with partially-concurrent solvent evaporation.

In order to fulfill the EU Guidance On Mineral Oil Analysis released in 2019, the results were expressed in sub-fractions (C-fractions), defined by using the position of the GC elution signals of 10 reference alkanes (from C_{10} to C_{50}). MOSH contamination was detected in all samples subjected to analysis at various levels, ranging between 2.4 and 375.7 ppm, with an average value of 49.9 ppm. Different C-fraction were detected, with the >C25-≤C35 range always presents with an average value of 26.9 ppm. All the samples analyzed resulted free of MOAH contamination, except for two samples for which a contamination at the 9.9 and 6.6 ppm levels was found.

Untargeted characterization and quantitative analysis of underivatized fatty acids in *Chlorella vulgaris* microalgae

Carmela Maria Montone, Sara Elsa Aita, Chiara Cavaliere, Andrea Cerrato, Aldo Laganà

Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy

Chlorella vulgaris is a popular microalga used for biofuel production. Nevertheless, it possesses a strong cell wall that complicates the extraction of molecules, especially lipids within the cell wall. Tackling this issue is crucial to develop an efficient and cost-effective method for optimal lipid extraction. A chemical method was applied and optimized for *Chlorella vulgaris* sample. Microalgae cell disruption by acid hydrolysis with sulfuric acid was investigated, comparing three temperatures (room temperature, 70 °C, and 140 °C) and three reaction times (60 min, 90 min, and overnight). After acid hydrolysis, lipids were extracted using n-hexane. Seven standard lipid species were spiked on dried microalgae biomass, and the hydrolysis percentage was calculated for each hydrolysis condition to choose the best one. The optimal condition was obtained at 140 °C after 90 min, for which the hydrolysis process was quantitative. The microalgae were then analyzed by an untargeted approach based on liquid chromatography coupled to high-resolution mass spectrometry. Twenty-eight fatty acids were tentatively identified. A quantitative analysis on the untargeted data was initially performed, using peak areas as a surrogate of analyte abundance for relative quantitation. Even though untargeted analysis is a powerful approach for the qualitative identification of complex mixtures, absolute quantification is necessary to obtain more reliable data and share the obtained results more straightforwardly from one laboratory to another. Then, a targeted quantitative method was validated for the tentatively identified fatty acids. Usually, quantitative analysis is carried out by low-resolution mass spectrometry-based on multi reaction monitoring (MRM) approach. The MRM approach disadvantages are linked to the limited number of targets and low-resolution mass spectrometry generally employed. Since FAs do not have a fragmentation pattern, HRMS was necessary for their identification to compensate for the lack of characteristic product ions at the MS/MS level. The method gave good recovery (78-100%), intra- and inter-day relative standard deviations (<10% and < 6%, respectively) and linearity (R2 > 0.98). The quantitative analysis confirmed the untargeted analysis's identifications and indicated that the most abundant fatty acids were palmitic, palmitoleic, oleic, linoleic, linolenic, and stearic acids.

This work was supported by the Italian Ministry of University and Research (MUR, Italy) under grant PON for industrial research and experimental development ARS01_00881, ORIGAMI: Integrated biorefinery for the production of biodiesel from microalgae.

Simultaneous Enantiomeric and Isotopic Ratio evaluation of target terpenes in Cannabis sativa essential oils through Enantio-MDGC-C-IRMS

Lorenzo Cucinotta[a,b], *Gemma de Grazia*[a], *Danilo Sciarrone*[a], *Luigi Mondello*[a,c,d,e]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b] *Department of Food Quality and Nutrition, Research and Innovation Centre, Fondazione Edmund Mach, via Mach 1, San Michele all'Adige, 38010, Italy;*
[c] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, 98168 Messina, Italy*
[d] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, 98168 Messina, Italy*
[e] *Department of Sciences and Technologies for Human and Environment, University Campus Bio-Medico of Rome, Rome, 00128, Italy*

Cannabis sativa L., belonging to the family of *Cannabaceae,* is an annual herbaceous plant, whose interest is ever-growing. Its essential oil, mainly constituted by monoterpene and sesquiterpene compounds, is nowadays a remarkable expensive product in food and perfumery industry. In this regard, due to its increasing demand, it is not surprising the presence on the market of adulterated oils, simulating the composition of natural ones mainly in terms of the characteristic terpene compounds. Although some evident sophistications in the volatile composition may be recognized by GC-MS analysis, more specific analytical methods needs to be applied for the discovery of newer fraudulent actions.

To these aims, the simultaneous detection of both the isotopic and enantiomeric ratio of key target compounds employing enantio-GC-C-IRMS can be considered a suitable approach to highlight the genuineness of natural samples.

Nevertheless, such a monodimensional approach shows limitations when peaks co-elute. An optimized separation is in fact mandatory for both the revelation systems, even more for IRMS, due to the different distribution of carbon isotopes along an entire peak of CO_2, which would lead to major errors in case of peaks overlapping.

In order to overcome these limitations, in the present study, an enantio-MDGC-C-IRMS method was developed employing an apolar column in the ^{1}D and a chiral CD-based stationary phase in the ^{2}D, evaluating both the enantiomeric and isotopic ratio of well-separated target terpenes in natural cannabis EOs.

For this purpose, genuine essential oils samples were obtained after microwave assisted extraction of fresh and dried inflorescences. The results were used as reference data to evaluate further commercial samples provided from local stores.

Evaluation of cryogenic effect for target VOCs isolation by a preparative multidimensional gas chromatographic system

Gemma De Grazia[a], *Lorenzo Cucinotta*[a, b], *Danilo Sciarrone*[a], *Paola Dugo*[a, d], *Luigi Mondello*[a, c, d, e]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b] *Department of Food Quality and Nutrition, Research and Innovation Centre, Fondazione Edmund Mach, via Mach 1, San Michele all'Adige, 38010, Italy;*
[c] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[d] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[e] *Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy*

The study describes the evaluation of the collection performance of volatile organic compounds with a wide range of boiling points and different polarity, exploiting a lab-made collection system under room temperature and cryogenic conditions. An efficient preparative-scale multidimensional gas chromatographic system was used, allowing the isolation of highly pure compounds at milligram levels. The system consisted of three Deans switch transfer devices and a set of mega-bore columns of different selectivity, i.e., 5% diphenyl-polyethylene glycol-ionic liquid stationary phases, affording both enhanced separation capabilities and reduced analysis time. Such an approach assured the sample capacity looked for preparative purposes, overcoming the well-known low efficiency of wide-bore columns, through an orthogonal combination of stationary phases. Thus, the study focused on optimizing the condensation of the analytes from the gas stream, after the chromatographic process, in relation to the different physicochemical properties of the target volatiles. As expected, specific collection conditions had a great influence on recovery values, depending on the different boiling points of the target compounds. A low-cost collection system was developed, enabling different operational configurations: specifically, both ambient and cryogenic conditions were tested for each VOC with the aim to evaluate the best temperature gradient, achieving satisfactory recovery degrees.

DEVELOPMENT OF A RAPID AND SIMPLE PROTOCOL FOR THE ASSAY OF PARABENS AND BISPHENOLS IN HUMAN SALIVA BY SOLID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-TRIPLE QUADRUPOLE MASS SPECTROMETRY

R. Elliani[a], *A. Naccarato*[b], *A. Tagarelli*[a]

[a]*Department of Chemistry and Chemical Technologies - University of Calabria, Via P. Bucci Cubo 12/C, I-87030 Arcavacata di Rende, CS, Italy;* [b]*CNR- Institute of Atmospheric Pollution Research, Division of Rende, c/o UNICAL- Polifunzionale, I-87036 Arcavacata di Rende, CS, Italy.*

The term "endocrine disruptor chemicals" (EDCs) refers to a group of chemical compounds which are able to interact with the endocrine system of a living organism. They were found in various materials such as pesticides, metals, additives or contaminants in food, and personal care products. Endocrine disruptors mainly alter the concentration of circulating hormones in the body, their synthesis, and their hepatic metabolism. The presence of EDCs is associated with an increased incidence of breast cancer, abnormal growth patterns and neurodevelopmental delays in children. The substances catalogued as EDCs includes synthesized chemical compounds and natural substances. Among them, specific classes include polycyclic aromatic hydrocarbons, pesticides, alkylphenols, dioxins, phthalates, parabens and bisphenols. Parabens are alkyl and aryl esters of *p*-hydroxybenzoic acid that are extensively employed as preservatives and bactericides in personal care products but also in processed food and beverages. Bisphenols are industrial chemicals used primarily as a flame retardant and stabilizer in the production of polycarbonate plastics, rubber, and epoxy resins. They are used in household appliances, in food packaging and also in toys for kids. Parabens and bisphenols show a certain estrogenic activity and toxic effect due to a continuous exposition by causing harmful effects on human health [1]. In this contest, a new analytical method for the assay of methylparaben, ethylparaben, propylparaben, butylparaben, benzyl 4-hydroxybenzoate, bisphenol AF, bisphenol F, bisphenol A, bisphenol S, bisphenol Z and bisphenol AP in human saliva was developed and optimized. The method provided an aqueous derivatization followed by solid phase microextraction-gas chromatography-triple quadrupole mass spectrometry (SPME-GC-QqQ-MS) analysis. The derivatization reaction provided the comparison of acetic anhydride [2] and alkyl chloroformate [3,4] as derivatizing reagents to obtain a selective and specific derivatization of the monitored analytes. The signals were recorded in selected reaction monitoring (SRM) acquisition mode that allows the achievement of high specificity by selecting appropriate precursor–product ion couples. The extraction ability of six commercially available SPME fibers was evaluated in univariate mode, while the use of "experimental design" (DoE) allowed the multivariate optimization of the variables affecting the SPME extraction and the derivatization reaction.

[1] Z. Petric, J. Ružic, I. Žuntar, *Acta Pharm.,* **2021**, *71*, 17-32.

[2] M. Pastor-Belda, L. Marín-Soler, N. Campillo, P. Viñas, M. Hernández-Córdoba, *J. of Chromatogr. A*, **2018**, *1564,* 102-109.

[3] R. Elliani, A. Naccarato, L. Malacaria, A. Tagarelli, *J. Sep. Sci*., **2020**, *43*,3061-3073.

[4] A. Naccarato, R. Elliani, B. Cavaliere, G. Sindona, A. Tagarelli, *J. Chomatogr. A*, **2018**, *1549*, 1-13.

Simultaneous determination of 88 multi-class pesticide residues in four vegetable matrices using reduced QuEChERS extraction and flow-modulated comprehensive two-dimensional gas chromatography-triple quadrupole mass spectrometry

A. Ferracane [a], M. Zoccali [b], P.Q. Tranchida [a], L. Mondello [a,c,d,e]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*

[b] *Department of Mathematical and Computer Science, Physical Sciences and Earth Sciences, University of Messina, Messina, Italy;*

[c] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*

[d] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*

[e] *Department of Sciences and Technologies for Human and Environment, University Campus Bio-Medico of Rome, Rome, Italy*

The aim of the work was the development of an analytical method for the simultaneous determination of 88 multi-class pesticides residues in vegetable samples using a reduced-scale QuEChERS (quick, easy, cheap, effective, rugged, and safe) extraction coupled to flow-modulated comprehensive two-dimensional gas chromatography-triple quadrupole mass spectrometry (FM-GC×GC-QqQMS). Targeted pesticides were determined in four different vegetable matrices namely: tomatoes, cucumbers, sweet red peppers, and iceberg lettuce. The proposed reduced-scale method involved the use of only 3 g of sample. Matrix-matched calibrations were carried out for all the samples. The validation procedure was performed to determine recovery, linearity, precision, limits of detection, and limits of quantification. The developed QuEChERS FM-GC×GC-QqQMS method is both simple, rapid and is sensitive enough for EU regulation purposes.

Evaluation of use of hydrogen as carrier gas in flow-modulation comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry

Micaela Galletta [a], Mariosimone Zoccali [b], Peter Q. Tranchida [a], Luigi Mondello [a,c,d,e]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b] *Department of Mathematical and Computer Science, Physical Sciences and Earth Sciences, University of Messina, Messina, Italy;*
[c] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[d] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[e] *Department of Sciences and Technologies for Human and Environment, University Campus Bio-Medico of Rome, Rome, Italy*

The present research is focused on the evaluation of the use of hydrogen as carrier gas within the context of flow-modulation comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry. All experiments were carried out by using the following column set: SLB-5ms [silphenylene polymer which can be considered equivalent in polarity to poly(5% diphenyl/95% dimethylsiloxane)] with dimensions 10 m × 0.25 mm ID × 0.25 µm d_f as first dimension column, while the second dimension column was an SLB-35ms (silphenylene polymer which can be considered equivalent in polarity to poly(35% diphenyl/65% dimethylsiloxane) with dimensions 2 m × 0.10 mm ID × 0.10 µm d_f.

Efficiency was measured in both the first and second dimension, under different experimental conditions, using both helium and hydrogen. After defining the optimum carrier gas conditions, mixtures of fatty acids methyl esters and pesticides were analyzed to measure resolution, again in the first and second dimension. Finally, a sample of diesel was analysed, with the overall separation evaluated to make final conclusions on the analytical performances.

LC-MRM/MS assay for the quantification of some hormonal proteins in serum and follicular fluid of women undergoing in vitro fertilization

Anna Illiano[1,2], Gabriella Pinto[1], Simone Luti[3], Alesandra Modesti[3] and Angela Amoresano[1]

1. Department of Chemical Sciences, University of Naples Federico II, 80126 Naples, Italy.

2. CEINGE Advanced Biotechnologies, University of Naples Federico II, 80145 Naples, Italy.

3 Department of Biomedical, Experimental, and Clinical Sciences "Mario Serio", University of Florence, Florence, Italy

Lifestyle changes following the post-war economic development reflect the choice of postponed maternity that together to the higher exposition to environmental risk factors induce an increasing request for medical assisted fertilization (IVF , ICSI). During the last years, scientists is focusing on the molecular characterization of follicular microenvironment surrounding oocytes to understand the mechanism underlying several fertility troubles and to maximize the success of assisted fertilizations. Recently, the imbalance in reactive oxygen species production in ovarian follicular fluid has been demonstrated to have a negative effect on female fertility due to the reduction of antioxidant defence mechanisms crucial in the oocyte maturation and pregnancy [1]. Actually, an increase of oxidative stress has been recently observed in sera and FF of women with ages over 35 years old [2]. Above this finding, the expression of adiponectin has been measured by Western blot as a result of an inflammation process induced by reactive oxygen species production [2].

In the present work, a LC-MS/MS method in multiple reaction monitoring (MRM) has been developed to propose a molecular assay for the quantification of several adipokines, e.g. adiponectin and leptin, together with its metabolic antagonist such as ghrelin. A comparison of expression of such proteins was performed both on FF and serum of women ranged between 30–42 years old and grouped in two main groups over and under 35 years of age.

The more highly selective and specific LC-MRM/MS approach aims to propose an alternative tool to ELISA tests to quantify in a single run more adipokines potentially expression of inflammatory status of follicular material in women subjected to the medical assisted fertilization protocols.

[1]. Luddi A. et al. *Antioxidants* **2020**, 9, 927.

[2]. Luti S. et al. *Mol Reprod Dev*. **2020**, 1–10.

Preliminary evaluation of Magnetic Nanoparticles for glyphosate contaminated water remediation.

Raghav Dogra [a], *Marco Roverso* [a], *Giuseppe Di Bernardo* [a], *Paolo Pastore* [a], *Sara Bogialli* [a]

[a] *Department of Chemical Sciences, University of Padua, Via Marzolo 1, 35131 Padova, Italy.*

Glyphosate (GLY) is one of the most disputed herbicides due to its extensive use and suspected toxicity. The widespread use across the globe may also lead to excessive accumulation with further contamination of water bodies, exceeding permitted limits. Herein, magnetically guided iron oxide nanoparticles (magnetite/maghemite) coated with polydopamine (PDA) and functionalized with different metal ions (Ti(IV), Cu(II) and Fe(III)), have been preliminary investigated for water refinement from GLY and as a possible solid phase extraction material for future analytical applications. The ideology takes advantages of the chemical properties of glyphosate in order to develop a proper absorption material with magnetic properties, facilitating remediation.

Experimentally, the magnetic nanoparticles were firstly obtained using different synthesis method, out of which the most favorable was the co-precipitation. Hence, nanoparticles were coated by self-polymerized PDA and further functionalized with different metal ions. Different coating time and protocols were tested and evaluated. The characteristic physical and chemical features of particles were evaluated by X-ray diffraction (XRD), FTIR spectroscopy, scanning electron microscopy (SEM), energy Dispersive X-Ray (EDX), transmission electron microscopy (TEM). Magnetic properties were assessed using an in-house test. Chemo-remediation, i.e. the affinity of produced nanoparticles towards glyphosate, was investigated by ion chromatography coupled to high resolution mass spectrometer (IC-HRMS). Experiments, performed in different conditions of GLY concentration, water sample volume and complexity of the matrix, showed promising results, demonstrating the strong adsorption of the analyte by the synthesized materials. Additionally, results suggested that the Ti(IV) functionalized nanoparticles exhibit an higher, specific and selective adsorption of GLY compared to the bare ones and nanoparticles functionalized with other metal ions. The magnetically driven approach is a fast and efficient way for the remediation of GLY contaminated water. These engineered nanoparticles have a huge future prospect in terms of sustainable green analytical chemistry and possible water remediation from other emerging contaminants like organophosphorus pesticides, in addition to as solid phase extraction materials.

[1] H. Heidari, B. Khosrowshahi, *et.al.*, *J Chrom. B*. **2019**, *1114–1115,* 24–30.
[2] B. S. Rodríguez, J. H. Borges, *et.al.*, *J Chrom. A*. **2015,** *1397,* 1–10.
[3] R. Zheng, S. Wang, *et.al*., *ACS Appl. Mater. Interfaces* **2015,** *7,* 15876–15884.
[4] S. Piovesana, A. L. Capriotti, *et.al.*, *Analytica Chimica Acta*, 2016, *909,* 67–74.

Evaluation of mercury content in red mullet (*Mullus barbatus*) muscle from the Adriatic Sea in relation to biological factors and sampling area: risk assessment for human consumption

Federico Girolametti [a], *Emanuela Frapiccini* [b], *Anna Annibaldi* [a], *Silvia Illuminati* [a], *Monica Panfili* [b], *Mauro Marini* [b], *Alberto Santojanni* [b], *Cristina Truzzi* [a]

[a] *Department of Life and Environmental Sciences, Università Politecnica delle marche, Via Brecce Bianche, 60131 Ancona, Italy;* [b] *Institute of Biological Resources and Marine Biotechnologies (IRBIM), National Research Council (CNR), Largo Fiera della pesca 2, 60125 Ancona, Italy*

Environmental pollution by mercury (Hg) is of great concern due to its toxic effects both in ecosystems and biota. Hg is bioaccumulated and biomagnified in the form of MeHg in the food chain [1] and its presence in fish included in the human diet has been linked to neurological damage (Minamata disease) and increased risk of myocardial infarction [2]. Herein, total Hg levels have been determined in muscle tissue of red mullet (*Mullus barbatus*) from the Adriatic Sea, during the 2018-2019 catching season in GSA (Geographical Sub Area) 17 area (Fig. 1a). Specimens have been grouped into 16 pools based on sex, reproductive stages (juveniles, adults, pre-spawning, post-spawning), and sampling area (coast or open sea). Total mercury content was quantified by thermal decomposition amalgamation atomic absorption spectrometry using a Direct Mercury Analyzer (DMA-1, Milestone, Sorisole, BG, Italy) [3]. Overall mean value was 0.20±0.15 mg kg^{-1} ww (from 0.03 to 0.62) (Fig. 1b). No statistically significant difference ($p>0.05$) was evidenced between Hg content in females (0.23±0.20) and males (0.17±0.07), while a statistically significant difference ($p=0.0223$) was found between specimens caught in the open sea (0.28±0.16) and in coastal areas (0.12±0.07). Investigation on Hg content in different reproductive stages showed a bell-shaped curve trend in female fishes, with a higher Hg content recorded in adult and spawning stages both in the coast and open sea samples (Fig. 1b). No statistically significant correlation ($p>0.05$) was found between Hg levels and the lipid content (3.29±2.43 %, from 0.44 to 7.87) in muscle tissue, although a negative trend was recorded in both male and female specimens. Finally, based on Directive 1881/2006/EU and amending regulation 420/2011/EU [4], which set the limit for Hg in *M. barbatus* at 1.0 mg kg^{-1} ww, it has been assessed that all analyzed specimens can be considered safe for human consumption.

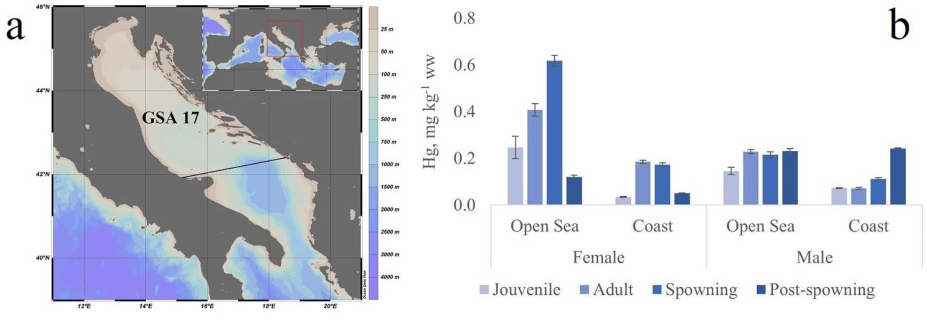


Figure 1. Sampling area (a) and Hg mean content (mg kg^{-1} ww) in *M. barbatus* (b).

[1] V. Celo, D.R. Lean, S.L. Scott, *Science of the Total Environment*. **2006**, *368*(1), 126-137.
[2] National Research Council. Toxicological effects of methylmercury. **2000**.
[3] A. Annibaldi, C. Truzzi, O. Carnevali, P. Pignalosa, P., M. Api, G. Scarponi, S. Illuminati, *Molecules*, **2019**, *24*(7), 1273.
[4] COMMISSION REGULATION (EU) No 420/2011 of 29 April 2011 amending Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs.

Experimental evaluation of Fenton oxidation coupled with membrane distillation for produced water treatment: benefits, challenges and effluent toxicity

Marco Minella[*a], Giulio Farinelli [b], Marco Coha [b], Debora Fabbri [a], Marco Pazzi [a], Claudio Minero [a], Davide Vione [a], Alberto Tiraferri [b]*

[a] *Department of Chemistry, Università di Torino, Via Pietro Giuria 5, 10125 Turin (Italy)*

[b] *Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129, Turin (Italy);*

The treatment of the wastewater resulting from the extraction of oil and gas - produced water (PW) - is a challenging task as this stream contains a large amount of contaminants and salts. Membrane distillation (MD) is a promising technology to desalinate hypersaline solutions such as produced waters. [1] However, due to the hydrophobic membranes used in MD, the large organic content of these waters can foul and wet the membranes, allowing for some fractions to pass into the distillate and impair its quality.

In this work, the application of the traditional Fenton process was preliminarily optimized and investigated as a pre-treatment step for a synthetic hypersaline PW, before the MD step. The traditional Fenton reaction was also compared to Fenton processes whereby iron ligands, e.g., Ethylenediamine-N,N'-disuccinic acid (EDDS) and citrate, were used to overcome practical limitations of traditional Fenton (e.g., the need to work at $pH \approx 3$). [2]

The oxidation pre-treatments achieved up to 55% removal of the dissolved organic carbon, measured as TOC, and almost complete degradation of the low molecular weight toxic organic contaminants. No increase in MD productivity was observed after the Fenton pre-treatment, but the final effluent had significantly improved quality in terms of organic content and toxicity, with EC_{50} values of up to 25 times higher than those measured for the raw PW. The addition of iron ligands during the oxidation step simplified the process, but resulted in an effluent having slightly lower quality in terms of toxicity compared to that obtained with traditional Fenton (Figure 1).

The coupled Fenton-MD process is a promising strategy to treat PWs for safe discharge in a streamlined train. Moreover, this investigation pointed to challenges that require further research advances.

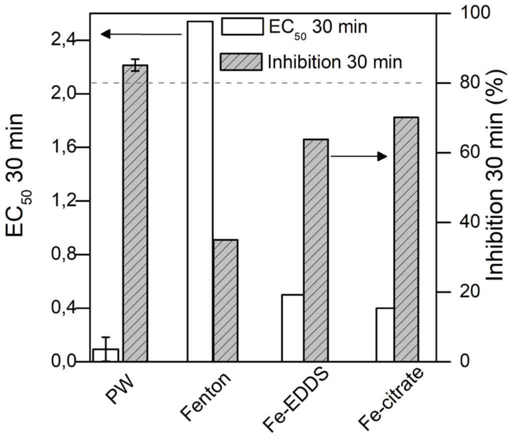


Figure 1 Residual toxicity (right axis) and EC_{50} (left axis) values after 30 minutes of contact with the *Vibrio Fischeri* culture for PW, and for PW after the coupled Fenton-MD process. The dash line (80% of inhibition) is the law limit for safe discharge in the sewage system in Italy.

[1] F. Ricceri, M. Giagnorio, G. Farinelli, G. Blandini, M. Minella, D. Vione, A. Tiraferri, *Sci. Rep.* **2019**, *9*, 14964.
[2] J.J. Pignatello, E. Oliveros, A. MacKay, *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 1.

Nanoconfined liquid phase nanoextraction: an innovative extraction technique for *ex-situ* and *in-situ* rapid and quantitative determination of benzene derivatives in seawater

Liyuan Wang[a], Huaze Sun[a], Chol-San Jon[a], Donatella Nardiello[b], Maurizio Quinto[a,b], Hai-Bo Shang[a], Donghao Li[a]

[a]Department of Chemistry, Yanbian University, Park Road 977, Yanji 133002, Jilin Province, PR China, [b]DAFNE - Department of Agriculture, Food, Natural resources and Engineering, University of Foggia, via Napoli 25, I-71122 Foggia, Italy

Benzene derivatives (BDs) constitute a class of environmental pollutants whose exposure poses a grave risk to human health [1]. These compounds rapidly diffuse from the atmosphere to the marine ecosystem: for this reason, their monitoring in seawater is every day more compelling [2]. In this work, nanoconfined liquid phase nanoextraction (NLPNE), a versatile extraction technique recently described [3], has been for the first time applied to the gas chromatographic mass spectrometry (GC/MS) analysis of BDs in seawater. *Ex-situ* and *in-situ* NLPNE procedures have been developed and optimized in terms of extraction capabilities, analysis time, precision, and accuracy. Compared to the traditional extraction procedures, based on solid-phase microextraction (SPME) and liquid-liquid extraction (LLE), the proposed NLPNE methods allowed a rapid on-site analysis of benzene compounds with low solvent consumption, higher enrichment factors, and improved automation grade. Our results suggest that NLPNE coupled to GC-MS can be considered a powerful technique for high-throughput analyses of trace compounds in environmental, food and biological samples.

[1]. D. Loomis, K.Z. Guyton, Y. Grosse, F. El Ghissassi, V. Bouvard, L. Benbrahim-Tallaa, N. Guha, N. Vilahur, H. Mattock, K. Straif, *The Lancet. Oncology*. **2017**, *18*, 1574.

[2]. L. Miller, X. Xu, A. Grgicak-Mannion, J. Brook, A. Wheeler, *Atmospheric Environment* **2012**, *61*, 305.

[3]. Y. Zou, L. Wang, H. Sun, G. Wang, L.-Y. Meng, M. Quinto, D. Li, *Anal.* **2021**, *93*, 1310.

Characterization of polyphenolic compounds in food and industrial wastes

Gabriella Pinto[a,b], Anna Illiano[a,b], Maria Anonietta Carrera[a]; Simonetta Caira[c], Francesco Addeo[d], Paolo Casoria[e], and Angela Amoresano[a,b]

[a] Department of Chemical Sciences, University of Naples Federico II, 80126 Naples, Italy.; [b] INBB, Istituto Nazionale Biostrutture e Biosistemi, Consorzio Interuniversitario, 00136 Rome, Italy; [c] Proteomics & Mass Spectrometry Laboratory, ISPAAM, National Research Council, via Argine 1085, 80147 Naples, Italy. [d]Agriculture Department, University of Naples Federico II, via Università 100, Parco Gussone, 80055 Portici, Italy. [e] Department of Sciences and Technology, University of Naples Parthenope, 80133 Naples, Italy

The production of any industrial output requires the need to sort out a large plethora of issues among which the disposal of processing waste in the view of reducing the impact of the by-products on the environment. Recycling operations are welcome to valorize the industrial wastes especially if the process by-products are organic material further exploitable as a potential source of energy and bioactive compounds.

During the last years, particular focus of our research group has been addressing at the characterization of a class of bioactive compounds *e.g.* polyphenols from different food matrices.

Polyphenols are a class of secondary metabolites produced by plants through the shikimate and acetate pathways. They are involved in the defense mechanisms against the ultraviolet radiation, drastic environmental conditions, insects, or pathogens and contribute to the organoleptic properties of fruits and leaves. Thanks to their phenolic structural features, polyphenols are efficient antioxidants and radical scavengers and, for this reason, they display huge health benefits when ingested through the diet, such as lowering blood pressure and plasma cholesterol levels. Recently, fifty polyphenols were detected by using LC-MS/MS in Multiple Reaction Monitoring (MRM) in the attempt to map chocolates made by cocoa beans of different geographical areas [1]. Forty polyphenols differently distributed in tea infusions at various fermentation levels as a result of the specific treatment of leaves were quantified by the similar targeted MS approach [2]. Further, the curing process of chestnut has been recently studied by *untargeted* mass spectrometry (MS) approach [3]. In the present work, total phenolic content (TCP) and polyphenol profiling of two different food matrices, such as apples and chestnuts, were explored by *targeted* and *untargeted* MS approaches. Such matrices are widely used in the industrial manufacturing for the fruit juice or cream preparation and their skin is wasted as industrial by-products. The final goal is to highlight the possibility of recycle such products by extracting bioactive compounds as a source of polyphenols for food, nutraceutical, leather, and cosmeceutical applications.

[1] G. Pinto, M. Aurilia, A. Illiano, C. Fontanarosa, G. Sannia, M. Trifuoggi, V. Lettera, R. Sperandeo, P. Pucci, A. Amoresano, *J Mass Spectrom* **2021**, *56*, e4651.

[2] G. Pinto, S. De Pascale, M. Aponte, A. Scaloni, F. Addeo, S. Caira, *Molecules* **2021**, *26*.

[3] G. Pinto, G. Picariello, F. Addeo, L. Chianese, A. Scaloni, S. Caira, *J Agric Food Chem* **2020**, *68*, 8744-8754.

Iterative protocols for the extraction and quantitation of microplastics from marine sediments and oysters

Luca Rivoira[1], Michele Castiglioni[1], Sabrina R. Rodrigues[2], Irene Ingrando[1], Sandra Ramos[2], Vania Freitas[2], Maria Concetta Bruzzoniti[1] and Cristina Marisa Ribeiro de Almeida[2]*

[1]Dipartimento di Chimica, Università degli Studi di Torino, Torino, Italy
[2]CIIMAR, Interdisciplinary Centre of Marine and Environmental Research University of Porto, Porto, Portugal

luca.rivoira@unito.it

Seas and oceans are nowadays recognized to be affected by microplastic (MP) pollution, with MPs commonly defined as plastic fragments particles having, in general, less than 5.0 mm length. Threat to marine ecosystems and human health are the main issues regarding MP pollution, with recently observed relation between the use of fishing nets and the presence of microfibers. These fibers could aggregate to originate clusters, which can precipitate contaminating marine sediments, or even be ingested by a wide range of marine organisms, including bivalves cultured for human consumption, such as oysters. Hence, the monitoring of the presence of MPs by proper protocols is still necessary. The National Oceanic and Atmospheric Administration (NOAA) proposes two distinct MP extraction protocols for sandy and bed sediments, which, however, have been shown to suffer from many limitations. Conversely, to what concerns oysters, published protocols are usually time consuming, requiring a KOH 24–48 hour oxidation step.

In this context, the aim of this study is to show how an iterative adaptation of the NOAA protocol allows the extraction of MPs from marine sediments, regardless of their characteristics. The method tested on PE-LD/PET/PA/PE-HD of different shapes (fragments, fibers and spheres) is based on density separation and oxidation treatments which were both carefully tuned. Final recoveries were higher than 85% for all the micropolymers (100% for PE and PA), avoiding any alteration of MPs polymer structure, necessary to proceed for a spectroscopic identification.

Furthermore, a new protocol for the extraction of MPs from oysters was derived, highlighting its efficacy (recoveries higher than 84% for all polymer types tested) and time-saving peculiarity (complete degradation of the organic matrix within 1 h).

Finally, both protocols were successfully applied in sediments collected from a fishing ground and close by a highly anthropic area (Porto, Portugal) and in oysters collected in an estuarine area, revealing the not negligible presence of many microfibers (Figure 1).

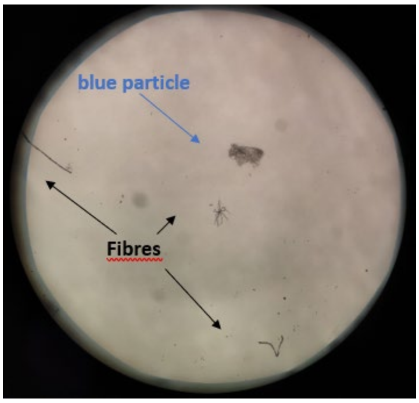


Figure 1: *MPs extracted from an oyster. The picture was taken by stereomicroscope, in B/W mode, using a 10X magnification.*

Acknowledgements: NetTag project (EASME/EMFF/2017/1.2.1.12/S2/02/S12.789121) and Framework Agreement For Scientific Cooperation #1534 Between Università Di Torino (Department of Chemistry) And Universidade Do Porto (CIIMAR - Interdisciplinary Centre of Marine and Environmental Research)

Validation of a new method for the simultaneous determination of different classes of PBT chemicals in biota samples

Saul Santini[a], Matteo Baini[b], Eleonora De Beni[a], Tania Martellini[a], Chiara Sarti[a], Maria Cristina Fossi[b], Alessandra Cincinelli[a]

[a] *Department of Chemistry "Ugo Shiff", University of Florence.*
[b] *Department of Environmental, Earth and Physical Sciences, University of Siena.*

Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), novel brominated flame retardants (NBFRs), phthalate esters (PAEs) have been widely used in the recent decades for many purposes. PCBs have been mainly used as coolants for transformers, hydraulic fluids and cutting oils[1], PBDEs and NBFRs as flame retardants[2,3], and PAEs as additives to make plastics more flexible and harder to break[4]. These organic chemicals are endocrine disruptors (EDs), cancerogenic, widely distributed in the environment and cause adverse effects on human health due to their persistent, bioaccumulative and toxic (PBT) properties[3,5]. The challenge of this research is to develop a new method to simultaneously determine different classes of PBT chemicals in different biota matrices, overcoming the matrix effect that usually causes serious problems with the quantification analysis.

When developing an analytical method, particular attention should be paid to the very low concentration at which these organic compounds occur in biota samples, the complexity of the matrix and the high amount of lipid content. The extraction and clean-up/preconcentration represent the most critical steps of the analytical process and play a key role in maximizing the recovery of the analytes and minimizing the matrix effect.

To this aim, a new method for PBTs analysis in biota samples by ultrasound-assisted extraction (UAE) combined with dispersive solid-phase extraction (d-SPE) as clean-up procedure was developed, optimized and validated by replicate analysis of a certified reference fish (N=5). The linearity of the method was evaluated by spiking labeled internal standards at different concentrations in 0.5 g d.w. of fish samples. The precision data, coefficient of variation (CV%), for the analytical method were calculated for each spike level by intra- and inter-day (5 consecutive days) method repetition. The limit of detection (LOD) and limit of quantification (LOQ) were evaluated by replicated (n = 5) analysis of procedural blanks. To investigate the matrix effect on linearity, the slope and intercept of the calibration curve were statistically compared by means of a Student's t-test at the 95% confidence level with those obtained by the analyses of the standard solutions in matrix extracts; the residual standard deviations were tested by an F-test at the 95% confidence level.

Finally, recoveries were determined for all labeled internal standards spike levels within the same workday.

[1] Buckman, *Aquat. Toxicol.* **2006**, 78, 176–185.
[2] Shanmuganathan, *Mar. Pollut. Bull.* **2011**, 63, 154–159 .
[3] McGrath, *Emerg. Contam.* **2017**, 3, 23–31.
[4] Salazar-Beltrán, *Food Anal. Methods*. **2018**, 11, 48–61.
[5] Braouezec, C., *Environ. Sci. Pollut. Res.* **2016**, 23, 9574–9584.

Study of iron speciation in coastal seawater samples of the Ross Sea (Antarctica) by CLE-AdSV

D. Vivado[a]*, F. Ardini*[a]*, P. Rivaro*[a]

[a] *Department of Chemistry and Industrial Chemistry, University of Genoa, Genoa, Italy*

Iron (Fe) is the most important trace element in the ocean, as it is required by phytoplankton for photosynthesis and nitrate assimilation, and it is the primary limiting micronutrient in the High Nutrient Low Chlorophyll (HNLC) region across large parts of the Southern Ocean. The solubility of Fe is increased above the solubility product of Fe-(hydr)oxides by complexation with dissolved organic ligands [1][2]. The most common method to measure Fe-binding organic ligands is the Competitive Ligand Equilibration-Adsorptive Stripping Voltammetry (CLE-AdSV), which allows to obtain the concentration of complexed and free Fe, of the ligands, and the values of the stability constants of the complexes [3][4][5].
Iron concentration and speciation were determined in 43 coastal seawater samples collected in the western Ross Sea (Antarctica) during the austral summer 2017 as part of CELEBeR (CDW Effects on glacial mElting and on Bulk of Fe in the Western Ross sea) project. Fe values ranged from 0.4 to 2.50 nM and log K'_{FeL} from 22 to 25, highlighting the presence of Fe-binding organic complexes of different stabilities. Principal Component Analysis (PCA) allowed us to explore the correlations between Fe species and the environmental parameters and to provide insight into the Fe biogeochemistry in the Ross Sea.

[1] E. Ibisanmi, S. G. Sander, P. W. Boyd, A. R. Bowie, and K. A. Hunter, "Vertical distributions of iron-(III) complexing ligands in the Southern Ocean," *Deep. Res. Part II Top. Stud. Oceanogr.*, vol. 58, no. 21–22, pp. 2113–2125, 2011.

[2] M. Gledhill and K. N. Buck, "The organic complexation of iron in the marine environment: A review," *Front. Microbiol.*, vol. 3, no. FEB, pp. 1–17, 2012.

[3] P. L. Croot, K. Andersson, O. Murat, and D. R. Turner, "The distribution and speciation of iron along 6 °E in the Southern Ocean," *Deep. Res. Part II*, vol. 51, pp. 2857–2879, 2004.

[4] L. J. A. Gerringa, S. Blain, P. Laan, G. Sarthou, M. J. W. Veldhuis, and C. P. D. Brussaard, "Fe-binding dissolved organic ligands near the Kerguelen Archipelago in the Southern Ocean (Indian sector)," *Deep. Res. Part II*, vol. 55, pp. 606–621, 2008.

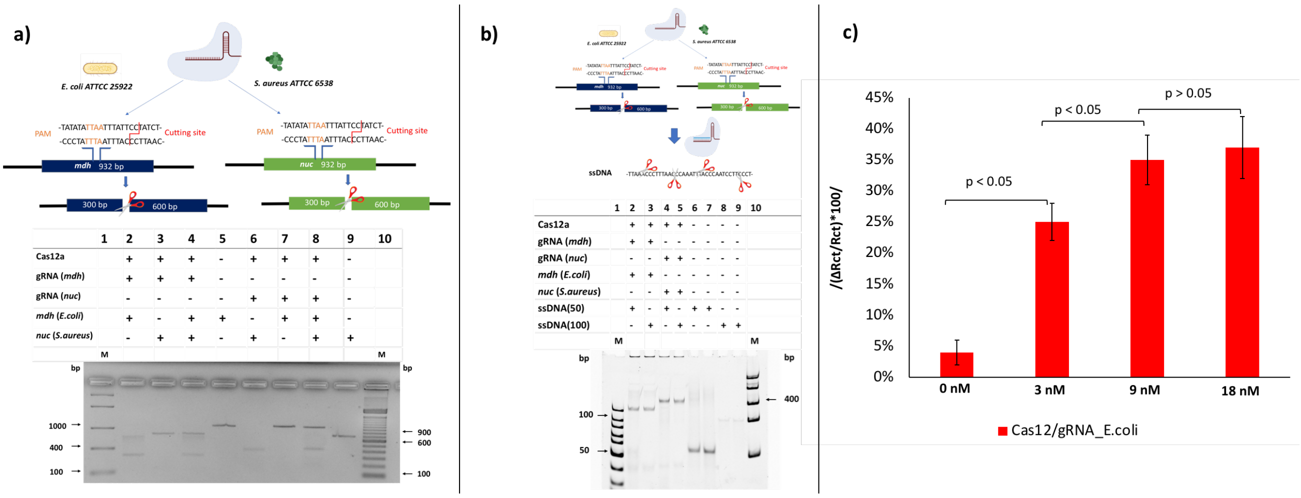
[5] L. M. Laglera and D. Monticelli, "Iron detection and speciation in natural waters by electrochemical techniques: A critical review," *Curr. Opin. Electrochem.*, vol. 3, no. 1, pp. 123–129, 2017.

A Label-free impedance biosensing assay based on CRISPR/Cas12a collateral activity for bacterial DNA detection

A. Bonini[a], N.Poma[a], F. Vivaldi[a], D. Biagini[b], D. Bottai[b], A. Tavanti[b], F. Di Francesco[a]

[a] *Department of Chemistry and Industrial Chemistry – University of Pisa, Via G. Moruzzi 13, Pisa, Italy;*
[b] *Department of Biology – University of Pisa, Via San Zeno 35-39, Pisa, Italy.*

The rapid and selective identification in the clinical setting of pathogenic bacteria causing healthcare associated infections (HAIs) and in particular blood stream infections (BSIs) is a major challenge, as the number of people affected worldwide and the associated mortality are on the rise. In fact, traditional laboratory techniques such culture and polymerase chain reaction (PCR)-based methodologies are often associated to high turnaround times, which justify the pressing need for the development of rapid, specific and portable point of care devices [1]. Recently, a new class of programmable endonuclease enzymes called Cas proteins associated to clustered regularly interspaced short palindromic repeat loci (CRISPR) has revolutionized molecular diagnostics. The use of Cas proteins in optical and electrochemical biosensing devices has significantly improved the detection of nucleic acids in clinical samples [2]. In this study, we present a CRISPR/Cas12a system coupled with electrochemical impedance spectroscopy (EIS) measurements to develop a label-free biosensing assay able to detect Escherichia coli and Staphylococcus aureus, two bacterial species commonly associated to BSI infections. The programmable Cas12a endonuclease activity, induced by a specific guide RNA (gRNA), and the triggered collateral activity were assessed in in vitro restriction analyses (Figure1 a,b), and evaluated thanks to impedance measurements using a modified electrode (Figure1c) [3]. The Cas12a/gRNA system was able to specifically recognize amplicons from different clinical isolates of E. coli and S. aureus with a limit of detection of 3nM and a response time approximately of 1.30 h. To the best of our knowledge, this is the first biosensing device based on CRISPR/Cas12a label free impedance assay.



	1	2	3	4	5	6	7	8	9	10
Cas12a		+	+	+	-	+	+	+	-	
gRNA (*mdh*)		+	+	+	-	-	-	-	-	
gRNA (*nuc*)		-	-	-	-	+	+	+	-	
mdh (*E.coli*)		+	-	+	+	-	+	+	-	
nuc (*S.aureus*)		-	+	+	-	+	-	+	+	
	M									M

	1	2	3	4	5	6	7	8	9	10
Cas12a		+	+	+	+	-	-	-	-	
gRNA (*mdh*)		+	+	-	-	-	-	-	-	
gRNA (*nuc*)		-	-	+	+	-	-	-	-	
mdh (*E.coli*)		+	+	-	-	-	-	-	-	
nuc (*S.aureus*)		-	-	+	+	-	-	-	-	
ssDNA(50)		+	-	+	-	+	+	-	-	
ssDNA(100)		-	+	-	+	-	-	+	+	
	M									M

Figure 1 a) Visualization of the CRISPR/Cas12a cleavage specificity on a 1% agarose gel; b) 10% PAGE in TBE 1X. The gel shows Cas12a collateral activity upon cleavage of a 50 or 100 nucleotides ssDNA reporter; c) EIS Biosensing assay calibration response of Cas12/gRNA Vs E. coli target. The plot reports the relative charge transfer resistance depending on E. coli target DNA concentration from 3nM to 18nM.

[1] D.R. Jenkins, *Med. (United Kingdom)*. **2017**, 45, 629–633.
[2] A. Bonini, N. Poma, F. Vivaldi, A. Kirchhain, P. Salvo, D. Bottai, A. Tavanti, F. Di Francesco, *J. Pharm. Biomed. Anal.* **2021**, 192, 113645.
[3] A. Bonini, N. Poma, F. Vivaldi, D. Biagini, D. Bottai, A. Tavanti, F. Di Francesco, A Label-free impedance biosensing assay based on CRISPR/Cas12a collateral activity for bacterial DNA detection, J. Pharm. Biomed. Anal. **2021**, (Under review).

Molecularly imprinted polymers-based impedimetric sensor for metal-ion mediated recognition of a dipeptide

T. Di Giulio, E. Mazzotta, A. Barca, T. Verri, C. Malitesta

Dipartimento di Scienze e Tecnologie Biologiche e Ambientali (Di.S.Te.B.A.), Università del Salento, Italy

Molecularly imprinted polymers (MIPs) are synthetic materials bearing binding sites able to selectively recognize target analytes with mechanisms like those implemented by biological receptors, enzymes and antibodies. The selective molecular recognition ability is conferred to these materials during their synthesis procedure: the polymer is first synthesized in the presence of a target analyte (acting as template), which is then removed to obtain imprinted sites, complementary to the target in shape, steric hindrance and functionalities[1].

MIPs have proven their potential as synthetic receptors in numerous applications ranging from chromatography to assays and sensor technology due to their inherent advantages compared to biological recognition systems include robustness, stability and lower costs[1], [2].

Two approaches are commonly used to produce a MIP, which are i) covalent imprinting (covalent linkage between monomers and template) and ii) non-covalent imprinting (hydrogen bonding, hydrophobic interactions, electrostatic and van der Waals forces). In the first case, the removal of the target from the polymeric matrix can be difficult and slow rebinding kinetics can be observed; in the second approach, non-specific interactions can compromise the formation of homogeneous imprinted sites leading to a weak imprinting effect. Moreover, molecular imprinting of biological molecules such as peptides, proteins and enzymes, still remains a challenge due to their susceptible three-dimensional conformation and the large number of functional sites which complicate the synthesis of imprinted sites[3].

Herein, we propose the electrosynthesis of MIPs for carnosine, a dipeptide chosen as model molecules, using Zn- and Cu-porphyrin as monomers (namely, Zn(II)- and Cu(II)-5,10,15,20-tetrakis(4-aminophenyl)porphyrin). This choice aims to take advantages from the strong affinity between the histidine group of the target and metal centers Zn and Cu, for achieving a metal-ion mediated interaction in resulting high-affinity MIPs, thus overcoming issues of conventional covalent and non-covalent imprinting approaches.

Metalloporphyrin-based MIPs are electropolymerized by Cyclic Voltammetry (CV). Different experimental conditions have been explored (scan number/rate, potential range, monomer:template ratio, electrolyte concentration, mixture of solvents) and the optimized ones consist in the application of a potential from 0 to 1.1 V vs SCE at 100 mV s-1 for 15 cycles in a solution of 0.1 mM metalloporphyrin containing 0.1 mM carnosine in ACN/H2O (9:1, v/v). The imprinted electrode is then washed in NaOH 50 mM, under stirring for 10 minutes, until the complete removal of carnosine from the polymeric matrix is achieved, as evidenced by CV and Electrochemical Impedance Spectroscopy (EIS) tests. Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) results showed successful deposition of metalloporphyrin polymeric layers for both porphyrins and suggested higher affinity between carnosine and Zn-porphyrin.

EIS was also used for rebinding studies demonstrating MIP-sensor ability to detect carnosine at concentrations up to 1 mM and to selectively interact with carnosine in the presence of other peptides. Test on lysate of nerve cells samples show that the sensor is potentially applicable in real matrixes.

[1] E. Mazzotta, S. Rella, A. Turco, and C. Malitesta, *RSC Polymer Chemistry Series*, **2018**, 1, 412–446.

[2] J. Erdòssy, V. Horváth, A. Yarman, F. W. Scheller, and R. E. Gyurcsányi, *TrAC - Trends Anal. Chem.*, **2016**, 79, 179–190.

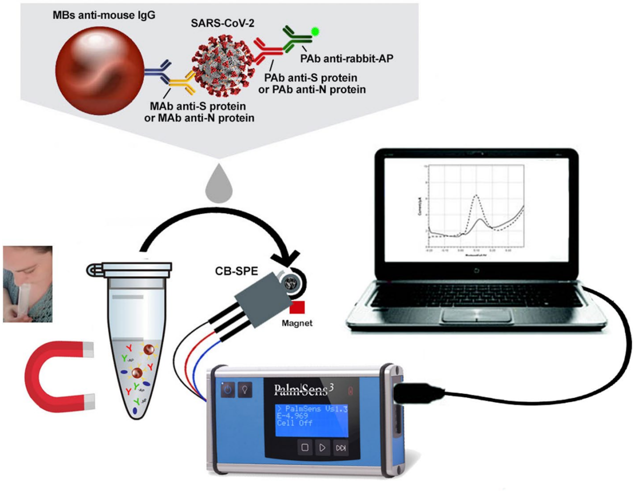
[3] J. Xu, P. X. Medina-Rangel, K. Haupt, and B. Tse Sum Bui, *Methods in Enzymology*, **2017**, 590, 115–141.

Magnetic beads combined with carbon black-based screen-printed electrodes for COVID-19: A reliable and miniaturized electrochemical immunosensor for SARS-CoV-2 detection in saliva

Laura Fabiani[a], Marco Saroglia[b], Giuseppe Galatà[c], Riccardo De Santis[d], Silvia Fillo[d], Vincenzo Luca[d], Giovanni Faggioni[d], Nino D'Amore[d], Elisa Regalbuto[d], Piero Salvatori[e], Genciana Terova[b], Florigio Lista[d], Fabiana Arduini[a,f], Danila Moscone[a]

a. *University of Rome "Tor Vergata", Department of Chemical Science and Technologies, Via della Ricerca Scientifica, 00133 Rome, Italy*
b. *University of Unsubria, Department of Biotechnologies and Life Sciences, Varese, Italy*
c. *GTS Consulting S.r.l., Via Consolare Pompea 1, 98168, Messina, Italy*
d. *Scientific Department, Army Medical Center, Rome, Italy*
e. *UOC, Army Medical Center, Rome, Italy*
f. *SENSE4MED, Via Renato Rascel 30, 00128, Rome, Italy*

The diffusion of novel SARS-CoV-2 coronavirus over the world generated COVID-19 pandemic event as reported by World Health Organization on March 2020. The huge issue is the high infectivity and the absence of vaccine and customised drugs allowing for hard management of this outbreak, thus a rapid and on site analysis is a need to contain the spread of COVID-19. Herein, we developed an electrochemical immunoassay for rapid and smart detection of SARS-CoV-2 coronavirus in saliva. The electrochemical assay was conceived for Spike (S) protein or Nucleocapsid (N) protein detection using magnetic beads as support of immunological chain and secondary antibody with alkaline phosphatase as immunological label. The enzymatic by-product 1-naphtol was detected using screen-printed electrodes modified with carbon black nanomaterial. The analytical features of the electrochemical immunoassay were evaluated using the standard solution of S and N protein in buffer solution and untreated saliva with a detection limit equal to 19 ng/mL and 8 ng/mL in untreated saliva, respectively for S and N protein. Its effectiveness was assessed using cultured virus in biosafety level 3 and in saliva clinical samples comparing the data using the nasopharyngeal swab specimens tested with Real-Time PCR. The agreement of the data, the low detection limit achieved, the rapid analysis (30 min), the miniaturization, and portability of the instrument combined with the easiness to use and no-invasive sampling, confer to this analytical tool high potentiality for market entry as the first highly sensitive electrochemical immunoassay for SARS-CoV-2 detection in untreated saliva.



Selective Single-Molecule Detection of clinically relevant biomarkers with an Organic Transistor

Eleonora Macchia,[a*] *Ronald Österbacka ,*[a] *and Luisa Torsi* [a,b,e]

[a] *The Faculty of Science and Engineering, Åbo Akademi University, FI-20500 Turku, Finland;* [b] *Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, 70125 Bari, Italy;*

* eleonora.macchia@abo.fi

The *US National Institute of Health* defines biomarkers *as molecules that can be objectively measured and evaluated as indicators of normal or disease processes and pharmacologic responses to therapeutic intervention*. Among the plethora of biomarkers, the sensitive detection of proteins is of paramount importance in a number of clinical fields.[1] The clinical use of protein biomarkers as indicators of the onset of pathological states requires the measurement of low concentrations of proteins in complex samples. Attempts to develop ultra-sensitive assays for the detection of protein biomarkers have been done by several groups in the last few years. Although in the last decade many approaches to achieve ultra-sensitive detection have been developed, most of them require complicated assay set-ups, hindering their adoption in point-of-care applications. In this perspective, Electrolyte-Gated Field-Effect-Transistors (EG-FETs) [2-6] with a bio-functionalized gate electrode, appear as very promising biosensing platforms. The EG-FET device herein presented, able to operate in physiologically relevant fluids such as blood serum and saliva, will set the ground to a major revolution in biosensing applications for early clinical detection.

[1] Barletta J.M. et al. **2004**, *Am. J. Clin. Pathol.*, 122, 20-27.
[2] Macchia E. et al. **2018** *Nature Communications*, 9, 3223.
[3] Macchia E. et al. **2019** *Chemistry of Materials*, 31, 6476–6483.
[4] Macchia E. et al. **2019** *Analytical and Bioanalytical Chemistry*, 411, 4899–4908.
[5] Macchia E. et al. **2020** *ACS Sensors*, 2020, 5, 1822–1830.
[6] Macchia E. et al., **2020** *Analytical and Bioanalytical Chemistry*, 2020, 412, 811–818.

Healthcare monitoring using wearable pH sensors

Federica Mariani [a], *Isacco Gualandi* [a], *Martina Serafini* [a], *Danilo Arcangeli* [a], *Francesco Decataldo* [b], *Luca Possanzini* [b], *Marta Tessarolo* [b], *Beatrice Fraboni* [b], *Domenica Tonelli* [a], *Erika Scavetta* [a]

[a] *Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy;* [a] *Dipartimento di Fisica e Astronomia, Università di Bologna, Viale Berti Pichat 6/2, 40127 Bologna, Italy*

Wearable chemical sensors are gaining momentum for the design of Internet of Things technologies and smart devices for personalised medicine, where real-time and non-invasive monitoring of biological parameters could dramatically impact on the quality of life. At the same time, essential sensor requirements such as conformability, robustness and simple architecture [1] are also shedding light on the limited applicability of conventional electrochemical sensors. On one hand, alternative sensing architectures based on organic electrochemical transistors (OECTs) have been showed to interface the biological domain providing intrinsic signal amplification, ease of miniaturisation and sensing capabilities without the need of a freestanding reference electrode. On the other hand, the design of novel electrochemical transducers allows to develop selective sensing devices and to realise innovative architectures that well adapt to flexible substrates and textiles. In this contribution, we report a material-based approach for the development of wearable pH sensors based on the organic semiconductor poly(3,4-ethylenedioxythiophene) (PEDOT) doped with the pH dye Bromothymol Blue (BTB). Upon functionalisation of the gate electrode of the transistor with PEDOT:BTB, a flexible OECT-based pH sensor was realised on a plastic foil for the non-invasive monitoring of sweat pH [2]. Furthermore, a simpler, electrochemically gated device was designed with a chemiresistor-like geometry, leading to facile integration into clothes or other real-life objects. The versatility and robustness of the two-terminal pH sensor architecture were demonstrated with the realisation of pH sensing textile yarns [3] and smart bioceramic fabrics [4] for real-time monitoring of sweat. Following this approach, our research group has recently optimised another PEDOT:PSS-based pH transducer, functionalised with Iridium Oxide particles, for the development of a smart dressing for improved wound healing management. In this case, the two-terminal device realized on medical bandages is able to monitor pH variations in simulated wound exudate, which could be correlated with the healing progression.

[1] I. Gualandi, M. Tessarolo, F. Mariani, L. Possanzini, E. Scavetta and B. Fraboni, *Polymers*, **2021**, *13*, 894.

[2] F. Mariani, I. Gualandi, M. Tessarolo, B. Fraboni and E. Scavetta, *ACS Appl. Mater. Interfaces*, **2018**, *10*, 22474.

[3] L. Possanzini, F. Decataldo, F. Mariani, I. Gualandi, M. Tessarolo, E. Scavetta and B. Fraboni, *Sci. Rep.*, **2020**, *10*, 17180.

[4] F. Mariani, I. Gualandi, D. Tonelli, F. Decataldo, L. Possanzini, B. Fraboni and E. Scavetta, *Electrochem. Commun.*, **2020**, *116*, 106763.

A TiO_2 /KuQuinone modified screen-printed photoelectrochemical sensor for NADH detection

V. Mazzaracchio[a], R. Marrone[a], M. Forchetta[a], F. Sabuzi[a,b], P. Galloni[a,b], M. Wang[c], K-L Choy[c], F. Arduini[a,d], D. Moscone[a]

[a] Dept. of Chemical Sciences and Technologies, University of Rome Tor Vergata,
Via della Ricerca Scientifica 1, 00133 Rome, Italy
[b] BT-INNOVACHEM, Via della Ricerca Scientifica 1, Rome, 00133, Italy
[c] UCL Institute for Materials Discovery University College of London, London, UK
[d] SENSE4MED, via Renato Rascel 30, 00128, Rome, Italy

Among the big plethora of analytical techniques, in recent years photoelectrochemical (PEC) sensing has witnessed rapid development despite a late start: thanks to the progresses of material science and nanotechnology, a series of advanced PEC methods have been developed and highly boosted.

The key feature of PEC sensing is the different energy forms between the excitation source (light) and detection signal (electricity), which enables advantages in terms of low background signal and higher sensitivity. Moreover, the implementation of electronic detection makes PEC instrumentation easy-to-use, inexpensive and miniaturizable.

The choice of the right photoactive material is the first step to design a high-performance PEC sensor: technology advances of nanoscience allow several semiconductors as photoactive materials to fabricate a versatile PEC biosensor, i.e. metal oxides (TiO_2, ZnO, WO_3, SnO_2, NiO) and transition metal chalcogenides (CdS, CdSe, CdTe, Ag_2S, MoS_2, PbS) heterostructures. Among the others, nanostructured TiO_2 has attracted increasing attention due to its high photosensitivity, good chemical stability, and low environmental impact.

On the other hand, a suitable sensitive material must be selected to increase or to modulate the properties of the photoactive material. Among the ones usually used, namely porphyrin, phthalocyanine, metal quantum dots, ruthenium(II) bipyridine, and inorganic semiconductors, a particular class of quinone, namely KuQuinones (KuQ) are characterized by high absorption coefficient, wide spectrum absorption spectrum range in the visible region, and a very low reduction potential. Moreover, they can be synthesized by a one-pot reaction, starting from reasonably cheap materials.

Herein we developed a TiO_2/KuQ modified graphite screen-printed electrode for the photoelectrochemical detection of NADH, i.e. an important enzymatic product of dehydrogenase enzymes class. In detail, the electrode was modified by drop-cast with a dispersion prepared by mixing a TiO_2/KuQ nanocomposites in DMF/water 1:1 (v/v).

Photocurrent generated measurements have been performed in presence of an electron donor specie in solution, namely NADH, applying a light source at 530 nm (i.e. LED source). Preliminary results demonstrated the suitability of the fabricated PEC sensing tool for the application in NADH detection, opening the way for the development of novel biosensors based on dehydrogenase enzymes.

The UCL Cities Partnerships Programme is highly acknowledged

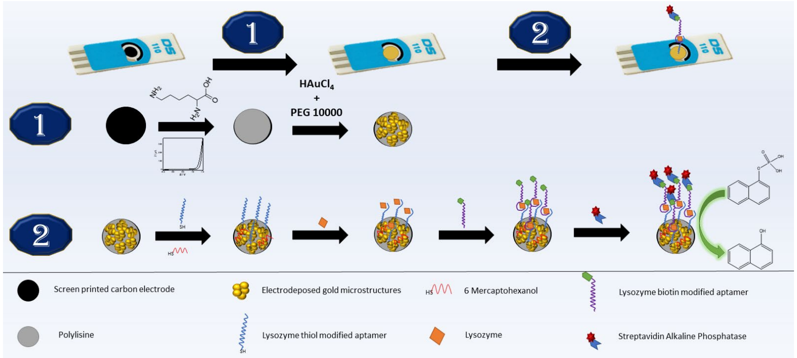
Enhancement of lysozyme detection process by using a gold clusters-based electrochemical aptasensor

Gheorghe Melinte[a,b], Oana Hosu[b], Geanina Ştefan[b,c], Cecilia Cristea[b], Giovanna Marrazza[a]

[a] "Ugo Schiff" Department of Chemistry, University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (Fi), Italy
[b] Department of Analytical Chemistry, "Iuliu Hatieganu" University of Medicine and Pharmacy, 4 Pasteur Street, 400349 Cluj-Napoca, Romania
[c] Robert Bosch SRL, Physical and Chemical Analysis Department (RBRO/EQV-A), Tetarom 3 Industrial Park, Jucu Herghelie 407352, Cluj, Romania

Lysozyme is an enzyme present in multiple organisms where it plays various vital roles. One of the most important relies on its antibacterial activity, being also called the body's own antibiotic. Despite its proven utility, lysozyme can potentially trigger allergic reactions in sensitive individuals, even in trace amounts, thus the need of continue monitoring of lysozyme in products rich in lysozyme like wine or egg white is of high importance.

In this work, an electrochemical aptasensor was designed for the flow analysis of lysozyme. First, poly-L-lysine was electrodeposited at screen printed carbon electrodes (SPCE) in order to obtain a more structured platform with higher electroactive area. The best architecture was further chosen for sensor development. Next, gold nanostructures were electrodeposited from a mixture of $HAuCl_4$ and PEG 10000 solution for enhanced electrocatalytic effect and to serve as immobilization platform for a thiolated aptamer. All platforms were electrochemically and morphologically characterized.



For lysozyme detection, a thiolated aptamer was immobilized at its 3'-end at the gold nanostructures surface, followed by a blocking step of the remaining free sites with 6-mercaptohexanol. Next, the affinity reaction with lysozyme was realised at the electrode surface and a second aptamer, labelled with biotin, was put in contact with lysozyme to obtain a sandwich assay. Further, streptavidin-alkaline phosphatase (ALP) reacted with the biotin bound to the second aptamer. The enymatic product, 1-naphtol, was subsequently triggered using differential pulse voltammetry to realise the lysozyme quantification. The aptasensor was succesfully applied in real samples, using different types of wine with very good recoveries.

Acknowledgements

Funds received from the Italian Government in the framework of PRIN 2017, Prot. 2017YER72 K_005 and UMF "Iuliu Hațieganu" Cluj-Napoca, for grant no. 1034/2/13.01.2021

Separation and Detection of Charged and Neutral Biomolecules in Plants and Food Matrices by Capillary Zone Electrophoresis

Danilo Corradini

CNR, Institute for Biological Systems, Area della Ricerca di Roma 1, 00015 Montelibretti (Rome), Italy (danilo.corradini@cnr.it)

Capillary Zone Electrophoresis (CZE), also known as free solution capillary electrophoresis, is an electromigration separation technique that uses continuous electrolyte solution systems and constant electric field strength throughout the length of a capillary tube, usually of fused silica, filled with an aqueous or nonaqueous background electrolyte solution. It is generally employed for microscale analytical separations of charged compounds, based on their electrophoretic mobility, that is the velocity at which charged compounds migrate toward the electrode of opposite sign in a considered medium per unit of the applied electric field. The methods mostly employed to separate uncharged compounds by CZE includes the use of a derivatization reaction performed before the electrophoretic separation or the incorporation into the BGE of a proper reagent capable to convert the neutral analyte into another charged molecule or complex.

This communication illustrates and discusses the results of the studies we have performed to investigate the use of selected additives, complexing agents, and organic solvents on the separation by CZE of biomolecules occurring in plants and food matrices. Both coated and bare fused-silica capillary tubes have been employed and the investigated additives, complexing agents, and organic solvents have been incorporated into the continuous background electrolyte solution (BGE) employed for the separations of biomolecules at various pH values. The observed effects on selectivity, resolution and separation efficiency of charged and neutral biomolecules of large interest in phytochemistry and food analysis are evaluated and discussed. Also reported and discussed are the effects of the investigated BGE compositions on the formation of the electric double layer at the interphase between the BGE and the inner surface of the fused-silica capillary tube employed for the separations, from which it originates the electroosmotic flow (EOF). All the investigated approaches have been carried out using continuous electrolyte solutions, whose optimal composition has been selected on the basis of experimental evidence. Examples of the discussed investigations include the study on the influence of trifluoroethanol incorporated into the BGE on the electrophoretic mobility of phenolic compounds separated by CZE as borate complexes. Also examined is the use of a strong alkaline BGE (pH 12-13) that allows neutral carbohydrates to be totally ionized, selectively separated as anions and directly UV detected as products of the photochemical reaction taking place in the detection windows. Applications of the discussed approaches to the separation of biomolecules in plant extracts and food matrices by CZE are illustrated and discussed.

Redox-active graphene film integrated into a smart device for pesticide biosensing

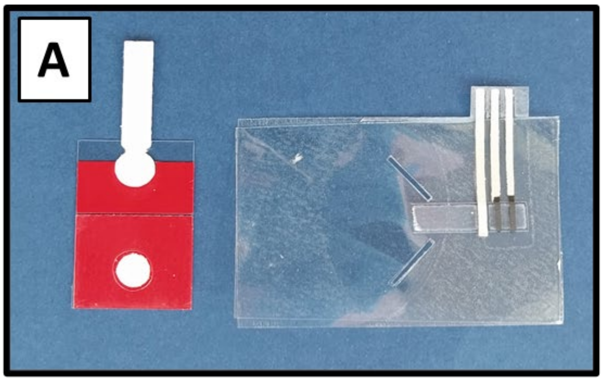
Filippo Silveri, Flavio Della Pelle, Annalisa Scroccarello, Qurat Ul Ain Bukhari, Dario Compagnone*

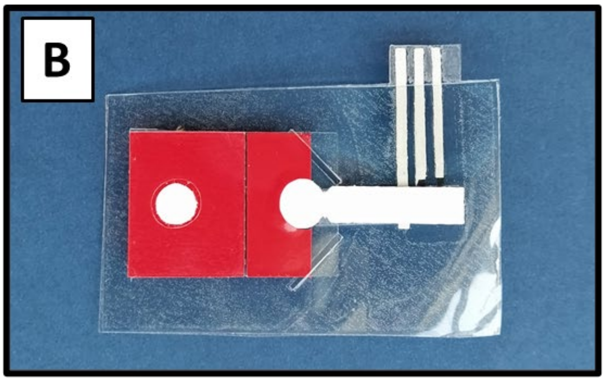
Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Campus "Aurelio Saliceti" via R. Balzarini 1, 64100 Teramo, Italy

Graphene-based materials have been extensively employed as electrode modifiers for the realization of sensors and devices. The 2D structure and the expected conductivity of graphene, make it prone to be assembled into self-supported films.

In this work, graphene water-soluble nanoflakes (GF) have been obtained by liquid phased exfoliation (LPE) of graphite, using catechin (CT) as a strategical stabilizing agent. The CT result able to assists graphene nanoflakes formation, integrating catecholic-adducts able to work as electrochemical mediators. GF-CT has been used to realize exclusively graphene-based nanofilms, realized onto thermal adhesive flexible PET sheets, via thermal transfer. GF-CT films showed well-defined reversible electrochemistry, attributed to the catecholic-adducts, resulting in a self-supported conductive film integrating a robust and reproducible electrochemical mediator.

GF-CT films showed electro-catalytic activity towards thiocholine, an enzymatic product derived from the activity of cholinesterase, allowing its mediated detection. Thus, the GF-CT film was exploited for the development of an integrated biosensor for the detection of chlorpyrifos, a widely used pesticide. The device, shown in **Figure A**, is composed of a module integrating the GF-CT film-based electrode, and by an interchangeable paper-based strip. The latter was designed to hosts the enzymatic reaction and allow the contact between the product (thiocholine) and the GF-CT film surface, by a paper strip. **Figure B** reports the device measure set-up, in which the paper strip is hosted in the plastic holder. Using the proposed device, chlorpyriphos was successfully analyzed in an inhibition assay format, totally occurring on the device. The device allows running the assay at low overpotentials (+0.2 V), ensuring a satisfactory LOD (0.2 ppb). The device, thanks to the smart design, allows realized 5 consecutive independent inhibition enzymatic assays (composed of pre and post inhibition measures), just by changing the paper strip, without losing performance (RSD 5.4%, n =5). Here, the marriage of nanotechnology with affordable manufacturing technologies brought to the realization a cost-effective (0.02 € per device) reusable device, usable even for on-field pesticide assessment.





Analytical approaches for safety assessment in the development of innovative packaging solutions

Antonella Cavazza[a,b], *Maria Grimaldi*[a], *Olimpia Pitirollo*[a], *Claudio Corradini*[a,b]

[a] *Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, Italy;* [b] *Centro Interdipartimentale per il Packaging, CIPACK, Parma, Italy.*

Since many years, high attention has been paid to migration of contaminants from food contact materials to products. In particular, controls aimed at safety assessment are needed in the field of packaging that is continuously developing new solutions.

Regarding plastic materials, the actual European regulation on Plastic Implementation Measures [1] provides the main analytical procedures to be followed in order to assure safety. Furthermore, innovative analytical approaches based on untargeted analysis, and aimed at the evaluation of the presence of non-intentionally added substances (NIAS), and emerging contaminants, have been developed [2-3].

This work describes some innovative solutions of active packaging based on the combination of different materials, and coating treatments on glass, wood, paper, and polymers, proposed to improve packaging performances. These treatments are often obtained using natural products, and are able to confer the materials new properties, such as antioxidant and antibacterial activity. In some cases, they even permit to achieve oxygen barrier or surface impermeabilization, allowing large applications in the field of food and cosmetics.

Coatings are generally complex systems, whose composition is not easy to assess, and therefore it is difficult to evaluate potential migrations, even when the raw materials used are known. In fact, new compounds may derive from chemical reactions occurring during the technological processes of coating deposition. Consequently, analytical untargeted approaches have been developed, and gas-chromatography coupled to mass spectrometry, with the help of chemical databases, was used to identify the chemical structure of the compounds.

A study related to the assembly of multiple materials, including secondary packaging, has also been performed, at first using simulants to perform untargeted analysis, then by building model systems, and finally analyzing packaged food products during shelf-life.

An important related field of research regards the necessity of replacing single-use plastic items according to the new European regulation on waste management [4], and it is focused on the development of alternative materials. The choice of natural substances, such as agricultural by-products, is selected as promising solutions, although the origin of these materials does not exclude the presence of harmful molecules [5-6]. Starting from these sources, some new materials in form of edible films and spray preparations have been formulated, and are proposed to prolong food shelf-life of meat and fish products.

[1] Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food. https://eur-lex.europa.eu/eli/reg/2011/10/oj
[2] M. Wrona, C. Nerin, *Molecules* **2020**, *25,* 752.
[3] A. Cavazza, C. Bignardi, M. Grimaldi, P. Salvadeo, C. Corradini, *Food Res Int*. **2021**, *139*, 109959
[4] Directive (EU) 2019/904 on the reduction of the impact of certain plastic products on the environment https://eur-lex.europa.eu/eli/dir/2019/904/oj
[5] L. Zimmermann, A. Dombrowski, C. Volker, M. Wagner, *Enironm Int*. **2020**, *145*, 106066.
[6] J. Nilsen-Nygaard et al., *Compr. Rev. Food Sci. F.* **2021**; *20*:1333.

Evaluation of the presence of plastics in two fish species of the Mediterranean Sea and potentially correlated harmful effects

Tatiana Chenet[a], Annalaura Mancia[b], Gioacchino Bono[c], Andrea Baldi[a], Alberto Cavazzini[a], Luisa Pasti[a]

[a] *Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, 44121, Ferrara, Italy;*
[b] *Department of Life Sciences and Biotechnology, University of Ferrara, Via L. Borsari 46, 44121, Ferrara, Italy;*
[c] *Institute for Biological Resources and Marine Biotechnologies, National Research Council (IRBIM-CNR), Via Vaccara 61, 91026, Mazara del Vallo (TP), Italy.*

The widespread diffusion of plastics in the environment, especially in the oceans, is an issue well known which is raising concern all around the world.

Plastics can break up in smaller pieces as a consequence of photo-degradation, physical fragmentation, and biological and chemical processes. Plastic debris are sorted according to their size, from nanoplastics (1 to 1000 nm) to macroplastics (1 cm and larger) [1].

Plastic particles can be ingested by marine organisms accidentally, but also because, due to their colour and shapes, they resemble natural food sources.

The ingestion of micro and macroplastics and their accumulation in the gastrointestinal tract (GIT) can lead to physical damage, but also to chemical adverse effects related to the release of toxic plastic additives or waterborne persistent organic pollutants adsorbed onto the plastic particles [2].

In this work we evaluated the presence of macro and microplastics in two species of the Mediterranean Sea: the Mediterranean small-spotted catshark (*Scyliorhinus canicula,* SC) and the Atlantic horse mackerel (*Trachurus trachurus,* TT). The fish were collected during the Spring 2018 in two geographic locations in the southern region of the Central Mediterranean Sea: near Mazara del Vallo and Lampedusa Island. The plastics isolated from the GIT of the fish, were sorted according to shape (fibres, filaments, and fragments), dimension, colour, and characterised by Raman spectroscopy to identify the polymer typology. Moreover, RNA was extracted from the spleen of the SC and the liver of TT specimens to investigate, via real time PCR analyses, the possible activation of immune response in SC and endocrine disruption in TT, possibly correlated to plastic ingestion.

The results showed that plastic ingestion is widely diffused in the two species from both locations, with microplastics (mainly polyester, polypropylene and polyamide) found in almost all the specimens analysed. Macroplastics (mainly polyethylene) were found with an average frequency of ingestion of 18% for SC both in Mazara del Vallo and Lampedusa, whereas for TT, macroplastics were found exclusively in a subset of larger specimens from Lampedusa.

Results from spleen and liver gene expression showed changes in the expression of three immune-related genes for SC specimens and anomalies in the production of vitellogenin in both males and females of TT.

Overall, our study suggests that the high frequencies of micro and macroplastics found in the two fish species considered could be a major cause for adverse effects in marine organisms, besides the interactions between the organisms and the wide variety of endocrine-disrupting substances present in seawater [2, 3].

[1] N. B. Hartmann *et al.*, *Environ. Sci. Technol.* **2019**, *53*, 1039 – 1047.
[2] A. Mancia *et al.*, *Mar. Environ. Res.* **2020**, *155*, 104876.
[3] T. Chenet *et al., Environ. Pollut.* **2021**, *in press*, 117449.

A Holistic Approach to the Characterization of High-Value Generating Molecules from the Wastes of Tuna Fishery Industry

Paola Arena[a]*, Francesca Rigano*[a]*, Domenica Mangraviti*[a]*, Danilo Donnarumma*[b]*, Paola Dugo*[a,b]*,*
Paola Donato[c]*, Luigi Mondello*[a,b,d]*, Giuseppe Micalizzi*[b]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[c] *Department of Biomedical, Dental, Morphological and Functional Imaging Sciences, University of Messina, Messina, Italy;*
[d] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

In the last decade, a progressive transition from the current linear economic model, to a more restorative system that drives substantial and lasting improvements of the global resource productivity has been registered. In this scenario, the circular economy promotes maximized use of resources and minimized waste production, through the re-utilization of industrial by-products as starting material for obtaining other products of economic interest.

A significant portion of the global fish trade is represented by tuna fisheries, and by-products resulting from the processing of raw materials into food products are usually discarded, generating a large amount of waste. A promising re-use of tuna wastes may concern their use as functional ingredients in the production of nutraceuticals for human consumption; in this regard, tuna by-products represent a valuable source of bioactive molecules, due to the significant content in ω3 and ω6 FAs, vitamins, minerals, amino acids, peptides and proteins.

In this research, the composition of the lipid and protein tuna fractions was investigated by the employment of a multitechnique analytical approach. An automated preparative station was coupled online to ultra-high performance liquid chromatography and tandem mass spectrometry (UHPLC-MS/MS) for the first time, allowing for sensitive and selective monitoring of different lipid classes. Similarly, automated sample preparation was exploited prior to fatty acid methyl ester (FAME) analysis by gas chromatography flame ionization and mass spectrometry detection (GC-FID/MS), by using a robotic platform. The automated sample preparation allowed to speed up the analytical workflow while providing a highly sensitive and selective lipid characterization.

Regarding the protein fraction, an isoelectric solubilization/precipitation (ISP) procedure followed by enzymatic hydrolysis and UHPLC-MS/MS characterization was successfully applied.

As a result, waste products showed a higher content in ω3 fatty acids compared to the muscle, both in terms of fatty acids and intact lipids. Furthermore, the use of bioinformatics tools highlighted the presence of potential antimicrobial peptides in the samples investigated.

Such knowledge provides a rationale for the use of bioactive molecules retrieved from the tuna supply chain in the design of micro- and nano-formulations as nutraceuticals with enhanced health benefits, increased bioavailability and patient compliance.

Insects food for the future

Federica Dal Bello[a], Enrica Mecarelli[a], Elisa Chessa[a], Claudio Medana[a]

[a] Department of Molecular Biotechnology and Health Sciences, University of Turin, via Pietro Giuria 5 - 10125 Torino

The world population has been increasing a lot in the past decades and new resource of foods are required. Insects are the key for the future. They are highly nutritive, have a high content of proteins and their production has little impact on the environment.

Entomophagy is practiced in many countries around the world, especially in Asia and Central America, while in Europe it is not practiced in the same way, both for issues related to the legislation that allows its circulation and consumption and for social and cultural issues.

Insects are labelled as “novel food”, that is, all those foods that have not been consumed "in a significant way" before May 1997 [1].

To ensure the safety of novel foods and the authorization of these products in the European market, evaluations of European and national bodies are necessary, including the scientific advice of EFSA (European Food Safety Authority), which has recently declared the safety of mealworm larvae (*Tenebrio molitor*) as novel food.

Allergies play an important role in assessing the safety of a food: almost all food allergies are related to proteins, therefore it is necessary to assess whether the consumption of insects can trigger allergic reactions in the consumer. These can be caused by individual sensitivity, by cross-reacting with other allergens or by allergens present in insect feed (such as gluten) [2].

The aim of the work was the development of a nanoHPLC-HRMS method for the determination of proteins known as allergenic in flour of cricket of species *Acheta domesticus*.

The sample preparation and purification steps required several tests to enhance the extraction of the proteins. The flour was treated with a sequential extraction to isolate the soluble proteins. At the end of the extraction, the proteins were subjected to tryptic digestion and then analyzed with a nanoHPLC instrument coupled to a high resolution mass spectrometer orbitrap Fusion.

For the bottom up analysis of cricket flour, a chromatographic separation lasting 250 minutes was set up using a nano-HPLC instrument and a chromatographic nano-column. Peptides belonging to some proteins already known as allergenic have been identified, including tropomyosin, present in the cricket in two isoforms, a known allergen present in crustaceans [3], and apolipophorin III, recognized as an allergen in the dust mite [4]. The work centered on the peptides deriving from the two tropomyosin isoforms. Following the selection of some marker peptides for tropomyosin I (3) and tropomyosin II (3) they were characterized thanks to the use of high resolution mass spectrometry. The tandem mass spectra were acquired in the three activation modes CID (Collision Induced Dissociation), HCD (High Collision Dissociation) and ETD (Electron Transfer Dissociation).

The next step of the work will be a comparison between allergens deriving from the whole insect and from flour using an optimized gel-electrophoresis and in gel digestion.

[1] Regulation (EU) 2015/2283 of the European Parliament and of the Council of 25 November 2015 on novel foods, amending Regulation (EU) No 1169/2011 of the European Parliament and of the Council and repealing Regulation (EC) No 258/97 of the European Parliament and of the Council and Commission Regulation (EC) No 1852/2001P.

[2] Thomas H. McConnell, The Nature of Disease: Pathology for the Health Professions. **2007**, Wolters Klumer Health, Lippincott Williams & Wilkins.

[3] J.K. James, *et al*. *Structure*, **2018**, *26*, 997-1006.

[4] Verhoeckx K.C.M, et al. *Food Chem. Toxicol*., **2014**, *65*, 364-373

Integrated approach for the analysis of some pesticides in vegetables and food matrices

Debora Fabbri[a], *Paola Calza*[a], *Anna Dioni*[a], *Marco Bergero*[b], *Barbara Guarino*[c], *Federica Dal Bello*[d], *Claudio Medana*[d]

[a] *Department of Chemistry, University of Turin, via Pietro Giuria 5, 10125 Turin (Italy);*
[b]*ASPROMIELE Via del Passatore 24/C - Fraz. S.Pio, Cerialdo - 12100 – Cuneo (Italy);*
[c] *Regione Piemonte, Assessorato Agricoltura, Settore Fitosanitario e S.T.C., Laboratorio Agrochimico, Via Livorno, 60 (Palazzina A2 L), 10144 Turin (Italy);*
[d] *Department of Molecular Biotechnology and Health Sciences, University of Torino, via Pietro Giuria 5, 10125 Turin (Italy)*

To protect harvest against destructive invertebrate pests efficiently, several insecticides have been developed and commercialized overcoming resistance issues and securing sustainable crop yields.

Once released into the environment, the pesticides may persist for long time or could undergo abiotic and biotic degradation processes [1] bringing to the formation of metabolites even more toxic than the parent compound. For such, in the present work we aimed to investigate the presence of three insecticides widely used, namely acetamiprid, sulfoxaflor and flupyradifurone and their transformation products in several samples of fruit, leaves, honey and pollen. These chemicals belong to different classes of pesticides, neonicotinoids, sulfoximines and butenolides respectively, although they share the same action mechanism as a receptor agonist toward nicotinic acetylcholine receptors (nAChRs).

Taking into account that studies on the investigated insecticides metabolites are scarce, the possible transformation products (TPs) were obtained and characterized by applying a laboratory simulation and then monitored in various vegetable matrices together with the pesticides themselves. This goal was obtained by using the photocatalytic process that has been already successfully used and applied to simulate transformation occurring in water and biological matrices [2, 3].

The laboratory simulation performed on sulfoxaflor has brought to the formation of three TPs while on flupyradifurone and acetamiprid leaded to the formation of seven and twelve TPs, respectively. Some of these identified TPs, characterized by HRMS, were found to coincide with known metabolites detected in vegetables, so implying that the applied approach can be employed to simulate metabolic pathways occurring in vegetables and food matrices.

In the examined samples, acetamiprid was detected at different concentration level in the honey, pollen and hazel leaves samples, in which also the presence of two TPs were observed. Sulfoxaflor was not detected, whereas flupyradifurone was found in honey samples, but the low concentration level did not allow detecting also their transformation products as we expect their formation at concentrations that are below the detection limit.

[1] B. Chaubey, P. Narwal, A. Khandelwal, S. Pal, *J. Photochem. Photobiol. A Chem.* **2021**, *405, 112986*.
[2] P. Calza, C. Medana, E. Padovano, V. Giancotti, C. Minero, *Environ. Sci. Pollut. Res.*, **2013,** *20 (4)*, 2262.
[3] C. Medana, P. Calza, V. Giancotti, F. Dal Bello, E. Pasello, M. Montana, C. Baiocchi, *Drug Test. Anal*. **2011**, *3*, 724.

Triacylglycerol Fingerprinting in Vegetable Oils by means of Subcritical Solvent Chromatography

Paola Donato [a], Marianna Oteri [b], Paola Arena [c], Luigi Mondello [c,d,e]

[a] *Department of Biomedical, Dental, Morphological and Functional Imaging Sciences, University of Messina, Messina, Italy;*
[b] *Department of Veterinary Sciences, University of Messina, Messina, Italy*
[c] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[d] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[e] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

Triacylglycerols (TAGs) are the major constituents of animal fats and vegetable oils and their dietary intake represents the main source of polyunsaturated fatty acids (PUFAs). Matrices composition, in term of TAGs, is responsible for the technological features of food products and determine the nutritional value, the physiological effects and the nutraceutical properties of foodstuff.

For these reasons, TAG analysis plays a key role in the characterization of food products, in confirming food authenticity and in detecting food fraud.

Reversed-phase liquid chromatography (RP-LC) represents the election separation mode for these apolar components, being the elution based on the increasing degree of hydrophobicity, commonly expressed in terms of partition number (PN) (depending on the total carbon number of the acyl chains, minus twice the number of double bonds).

On the other side, SFC is widely used for lipid analysis, showing the considerable advantage of the reduced organic solvent consumption with respect to LC, which determine a consistent reduction of costs, and a limited environmental impact: concepts that perfectly fits with green chemistry purposes.

Furthermore, the low mobile phase viscosity and higher diffusion coefficients allow for faster or more efficient separations.

The aim of this research has been the characterization of the TAG profile in vegetable oils, using CO_2 as the main mobile phase solvent, under subcritical conditions. The coupling to quadrupole time of flight (Q-ToF) MS detection allowed for average parameters of FA composition to be derived, in the oil TAG constituents identified. Different experimental parameters as nature and percentage of modifier into compressed CO_2, elution mode, gradient steepness pressure of the active backpressure regulator and column temperature were evaluated in this research.

The drawbacks of NARP-LC methods consisting in relatively long run times and the use of toxic solvents were overcome by the employment of a SFC system and the detailed profiling of TAG constituents in borage, corn, hazelnut, olive, palm, peanut, and soybean oils was achieved in a reliable and accurate manner.

Exploring the potentiality of capillary ion chromatography (CIC) as analytical technique for the determination of food additives

Marco Iammarino, Giovanna Berardi, Teresa D'Amore, Valeria Vita, Aurelia Di Taranto

Chemistry Department, Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata, Foggia, Italy

Ion Chromatography has become the most diffused analytical technique for the determination of ionic and ionizable compounds, not only in environmental applications, but also in food and drugs safety field. Compared to other available approaches, ion chromatography often results as a more simple, selective and robust technique. In the last years, the introduction of capillary ion chromatography (CIC) represented an improvement in the field, due to extremely reduced consumption of reagents which makes it very interesting with a view to the "Green Chemistry".

In this study, this analytical technique was applied for the determination of the most important food additives, such as nitrite, nitrate, sulphites, sorbic acid and benzoic acid, in food. After development and validation, where possible, these new analytical methods have been compared to the traditional ones, in terms of applicability, accuracy, robustness and management.

The analytical method for the determination of nitrite and nitrate was applied for the analysis of meat, fish and dairy products, animal feed, cereals, vegetables, fruit, legumes, seeds and dried fruit. The method is characterized by high accuracy (CV% < 3.4%, recovery: 98.8% - 100.8%) and good sensitivity (limits of detection: 1.20 and 0.68 and limits of quantification: 3.65 and 2.07 mg kg^{-1} for nitrite and nitrate, respectively). If compared to the traditional ion chromatography method, this novel approach results as more selective, since it is characterized by the full chromatographic separation between chloride/nitrite and sugar phosphates/nitrate **[1]**.

The analytical method for the determination of sulphites was applied for the analysis of wine, meat products and seafood. The method is characterized by excellent accuracy (CV% < 1.6%, mean recovery: 97.8%) and good sensitivity with quantification limit lower than 10 mg L^{-1} **[2]**.

Finally, regarding the determination of sorbic and benzoic acid, the analytical method developed is characterized by high accuracy (CV% < 2.5%, recovery: 92.2% - 97.6%) and good sensitivity (limits of detection: 1.6 and 4.9 and limits of quantification: 4.1 and 12.6 mg kg^{-1} for sorbic and benzoic acid, respectively). Thanks to the validation study, the method was applied for the analysis of fresh and processed fruit and vegetables, jam, sauces, soups, spices, dairy products and beverages, successfully **[3]**.

In conclusion, given the reduced consumption of reagent and the good validation parameters obtained, CIC can be considered as a valid alternative for the official food control activity related to the determination of food additives in most consumed foodstuffs.

[1] D'Amore T., Di Taranto A., Vita V., Berardi G., Iammarino M. (2019). Development and validation of an analytical method for nitrite and nitrate determination in meat products by Capillary Ion Chromatography (CIC). Food Analytical Methods 12, 1813-1822.

[2] Iammarino M., Di Taranto A., Centonze D. (2017). Determination of sulphiting agents in raw and processed meat: comparison between a modified Monier-Williams method and the direct analysis by ion chromatography with conductometric detection. Food Analytical Methods 10, 3956-3963.

[3] D'Amore T., Di Taranto A., Vita V., Berardi G., Iammarino M. (2019). Going green in food analysis: A rapid and accurate method for the determination of sorbic acid and benzoic acid in foods by capillary ion chromatography with conductivity detection. LWT – Food Science and Technology 141, 110841.

This work was supported by Ministero della Salute (Rome, Italy), who financed the project IZSPB 07/20 RC.

Use of ultra-high performance liquid chromatography to characterize non-volatile compounds in Italian beers

Fabio Salafia[a,*], *Rosa Di Sanzo*[a], *Sonia Carabetta*[a], *Pietro Andronaco*[a], *Mariateresa Russo*[a]

[a]*Food Chemistry, Safety and Sensoromic Laboratory (FoCuSS Lab), Department of Agriculture, University "Mediterranea" of Reggio Calabria, Via dell'Università, 25, 89124 Reggio Calabria, Italy.*

**fabio.salafia@unirc.it*

The consumption of beer, in recent years, has increased in all economically advanced regions, especially in countries where there is no old beer culture, such as France, Italy and Spain.

This phenomenon caused the development of new industrial beers, produced by multinational companies, and the birth of a large number of independent breweries [1].

The aim of this study was to identify and quantify minor compounds in beer, such as α-acids, β-acids and polyphenolic compounds, using them as quality markers of beers.

The method was developed with an ultra-high performance liquid chromatography reverse phase system, coupled to a UV-photodiode array detection detector.

The analysis were carried out using a binary mobile phase composed of an aqueous solution acidified with 0.1% (v/v) formic acid and a solution of acetonitrile acidified with 0.1% (v/v) formic acid with gradient elution mode. The analytes were separated with a C18 stationary phase column with a particle diameter of sub-2μm. Short analysis times and high chromatographic efficiency were obtained under these analytical conditions.

The separation conditions have been optimized considering the best basic separation of all the standard compounds considered.

The quantification was carried out with the calibration curves of the relative standards, the method was validated for each analyte with the parameters of LOD, LOQ, R^2 and CV%.

The method, developed and validated, has been used for the analysis of different industrial and craft beers. The analyzes were carried out in triplicate, the final result considered was the average of the values obtained.

Multivariate statistical analysis was used to determine the applicability of selected compounds as potential quality indicators of beers.

[1] B. Wojtyra, T. M. Kossowski, M. Březinová, R. Savov, D. Lančarič, *Appl. Geog*r. **2020**, *124*, 102325.

Characterization of volatile and non volatile compounds in citrus beer to evaluate product quality for food frauds prevention.

Emanuela Trovato[a], *Adriana Arigò*[b], *Federica Vento*[a], *Paola Dugo*[a,b], *Luigi Mondello*[a,b,c,d]

[a]*Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, 98168, Messina, Italy*

[b]*Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, 98168, Messina, Italy*

[c]*Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, via Alvaro del Portillo 21, 00128, Rome, Italy*

[d]*BeSep S.r.l. c/o Department of Chemistry, Biological, Pharmaceutical and Environmental Sciences, University of Messina, 98168, Messina, Italy*

In the last few years, consumers showed a growing interest in flavored beer market, and the assumption of citrus flavored beers has increased significantly.

The absence of a specific legislation concerning beer production and ingredients reported on the labels makes these beers subject to possible adulterations. Producers in fact are not obliged to specify if peel, juice, pulp, essential oils or hydro alcoholic extracts is used for the flavoring addiction process as natural ingredient.

Moreover citrus fruits contain oxygenated heterocyclic compounds; among them, furocoumarines are well known for their phototoxic reactions. However, there is not a regulation concerning their use in food, with possible dangerous effects for consumers' health.

Combining the volatile and non-volatile beer profile characterization is a powerful tool to identify markers of authentic citrus flavor, in order to compare the obtained data with the ingredients reported on the labels and discover possible frauds.

The linear retention indices were applied for both gas chromatographic and liquid chromatographic identification, as additional parameters to electron impact and tandem mass spectra, respectively.

Several commercial and crafted citrus flavored beer were analyzed, including samples in which lemon, bergamot, mandarin or orange peel/essential oils have been added during the brewing process, and few "radler" beer containing lemon juice. Non flavored and spiked samples were used as control.

The analysis carried out showed in many cases both the volatile and the oxygen heterocyclic compound profiles did not match those of the labeled citrus; furthermore in other samples even typical markers were not detected.

Despite the variables involved in the final beer composition are various and depending by different production steps, this study underline how the cross information given by the GC and LC characterization, both supported by the LRI system and libraries, can be applied for food quality control and fraud prevention.

Automate chemometric approach for peak identification and quantification in untargeted GC-MS data

Giacomo Baccolo[a,b], Beatriz Quintanilla-Casas[c,d], Davide Ballabio[a], Rasmus Bro[b]

[a] *Milano Chemometrics and QSAR Research Group, Department of Earth and Environmental Sciences, University of Milano - Bicocca, Milano, Italy.*

[b] *Department of Food Science, University of Copenhagen, Rolighedsvej 30, DK-1958 Frederiksberg C, Denmark.*

[c] *Departament de Nutrició, Ciències de l'Alimentació i Gastronomia, Campus de l'Alimentació Torribera, Facultat de Farmàcia i Ciències de L'Alimentació, Universitat de Barcelona. Av Prat de La Riba, 171, 08921, Santa Coloma de Gramenet, Spain.*

[d] *Institut de Recerca en Nutrició i Seguretat Alimentària (INSA-UB), Universitat de Barcelona. Av Prat de La Riba, 171, 08921, Santa Coloma de Gramenet, Spain.*

Untargeted chemical profiling is a widely used approach in several research field such as metabolomics, foodomics, systems biology and environmental analysis. The untargeted approach aims to achieve a complete characterization of the investigated samples, theoretically the aim is to identify and quantify every compound in the samples. Often the analysis involves complex matrices, such as biological tissues, foods or soil samples [1]. In this context, Gas Chromatography coupled to Mass Spectrometry (GC-MS) is broadly applied to analyze mixtures of small compounds [1].

The data acquisition is followed by the identification and quantification of the peaks among the different samples. This step results in a peak-table, which is the cornerstone for all the further analysis. Because of the complexity of the sample matrices, it is difficult to optimize the experimental conditions and obtain perfectly resolved peaks. The most common problems include baseline drift, peak shift among different samples and coelution of different compounds.

A number of tools, both commercial, such as ChemStation® from Agilent™, or freely available [2] have been developed in the context of GC-MS data analysis. These tools can be split into two groups that either analyze single sample or methods that take into account all the samples at the same time.

Here, we propose a new approach that belongs to the latter. In particular, our approach is based on a multiway deconvolutional model called PARAllel FACtor analysis2 (PARAFAC2) [3].

This modelling approach decompose the multilinear data finding the different signals across the samples based on collinearity. The PARAFAC2 model can easily handle both time and peak shape shifts and it has been widely showed the effectiveness of PARAFAC2 to extract meaningful chemical signals from GC-MS data [4].

Because of the intrinsic properties of the model and contrary to the common software for GC-MS analysis, PARAFAC2 has almost no need for data preprocessing and the results are fully user independent, while other tools require to set several parameters and a laborious pretreatment of the data, dramatically reducing results reproducibility.

However, the application of PARAFAC2 involves several steps and requires skilled tensor analysts. Here, we develop an expert system able to handle all the modelling steps and to generate a peak table with no redundancy. To test our approach, we used a complex dataset of 162 virgin olive oils with different quality grades, whose volatile profiles were obtained by solid-phase microextraction - GC/MS [5].

The peaks tables generated by the automatic analysis and the manual analysis carried out by experienced users have been compared. The results indicate that our approach overcome the manual analysis both in terms of number of identified compounds and quality of the identification and quantification.

[1] R. Tauler, H. Parastar, *Angew. Chemie Int. Ed.* **2018,** doi:10.1002/anie.201801134.
[2] S. O'Callaghan et al., *BMC Bioinf.* **. 2012** 1, 18.
[3] H.A.L. Kiers, , J.M.F. ten Berge, and R. Bro, *J. Chemom.,* **1999,** 13.3, 4.
[4] L.G. Johnsen et al., *J. Chromatogr. A,* **2017**, 1503, 57**.**
[5] B. Quintanilla-Casas et al., *Foods*, **2021**, 9(10), 1509

Oxylipin storm in COVID-19:
a new perspective in classifying disease severity

Denise Biagini[a], *Silvia Ghimenti*[a], *Tommaso Lomonaco*[a], *Andrea Bonini*[a], *Federico Vivaldi*[a], *Paolo Oliveri*[b], *Maria Franzini*[c], *Aldo Paolicchi*[c], *Alessandro Celi*[d], *Fabrizio Maggi*[e], *Roger Fuoco*[a], *Fabio Di Francesco*[a]

[a] *Department of Chemistry and Industrial Chemistry, University of Pisa, Italy; Department of Pharmacy (DIFAR) University of Genova, Italy;* [c] *Department of Translational Research on New Technologies in Medicine and Surgery, University of Pisa, Italy;* [d] *Department of Surgery, Medicine, Molecular Biology, and Critical Care, University of Pisa, and Respiratory Medicine Unit, Pisa Hospital, Italy;* [e] *Department of Medicine and Surgery, University of Insubria, Italy.*

Over 160 million reported cases and over 3 million deaths have been globally ascribed to the ongoing coronavirus disease (COVID-19) pandemic. About 15% of COVID-19 cases are severe and require hospitalization for oxygen supplementation, and 3–5% of these need admission to the intensive care unit (ICU) for ventilation support [1]. Many questions on both therapy and clinical management of COVID-19 patients remain open. Particularly, a critical care triage that prioritizes patients for intensive care, thus rationing limited ICU resources, is strongly required. Immune-inflammatory markers, which come from both cytokine and oxylipin storms, represent potential candidates as physiological prediction scores. Oxylipins are bioactive lipids generated from both ω-3 and ω-6 polyunsaturated fatty acids (PUFAs) through enzymatic (e.g., prostanoids, epoxy and hydroxy fatty acids) and non-enzymatic (e.g., isoprostanes) oxidation reactions [2]. During the course of inflammation, oxylipins switch from pro-inflammatory effectors to both anti-inflammatory and specialized pro-resolving lipid mediators (SPM), which could lower the inflammatory response and even promote its resolution. In light of this, a better understanding of the oxylipin storm is expected to provide new insights into the complex inflammatory cascade induced by SARS-CoV-2, thus leading to novel strategies for the management of COVID-19.

In the present work, a very powerful analytical platform, based on micro-extraction by packed sorbent (MEPS) coupled to liquid chromatography-tandem mass spectrometry (UHPLC-ESI-MS/MS) [3], was proposed for the determination of 60 plasmatic oxylipins in COVID-19 patients. A chemometric approach was employed to compare inflammatory metabolites coming from both cytokine and oxylipin storms between ICU and non-ICU patients. Unlike cytokines, oxylipins provided such a clear separation between ICU and non-ICU patients, when considered in a multivariate way by principal component analysis (PCA). Moreover, the presence nearby the ICU-cluster of subjects who would have ended up in ICU from 1 to 4 days after the oxylipin quantitation, suggested a potential predictive role of our panel of lipid mediators. To further confirm the power of the oxylipin pattern in separating patients based on disease severity, a multivariate ROC curve was obtained by application of the UNEQ class-modelling strategy [4-5], thus showing an area under the curve equal to 0.92. As far as we know, our observational study is the first one to report on an inflammatory response dysfunction discriminating between ICU- and non-ICU patients, suggesting the importance of targeting the lipid mediator class switching for a timely picture of the patient ability to respond to SARS-CoV-2 infection.

[1] W.J. Guan, et al., *N. Engl. J. Med.* **2020**, *382*, 1708–20.
[2] J.M. Galano, et al., *Prostag. Oth. Lipid M.* **2013**, *107*, 95-102.
[3] D. Biagini, et al., *Talanta.* **2020**, *216*, 120979.
[4] M.P. Derde, D. L. Massart, *Anal. Chim. Acta*. **1986**, *184*, 33–51.
[5] V. Pirro, *Bioanalysis*. **2013**, *5(6)*, 687–699.

Authentication of donkey's milk by Near Infrared Spectroscopy coupled with chemometric classifiers

Francesca Di Donato[a], *Alessandra Biancolillo*[a], *Alessandra Ferretti*[b], *Federico Marini*[b], *Angelo Antonio D'Archivio*[a]

[a] *Department of Physical and Chemical Sciences, University of L'Aquila, Via Vetoio 67100, Coppito, L'Aquila, Italy;* [b] *Department of Chemistry, University of Rome "La Sapienza", Piazzale Aldo Moro, 5, 00185, Roma, Italy*

Donkey's milk is attracting growing interest in human nutrition as a valuable alternative in feeding infants affected by cow's milk protein allergy, because of its similarity with human milk and its hypoallergenic properties [1]. In addition, it stimulates the immune system, regulates the gastrointestinal flora, and prevents inflammatory diseases [2]. Thanks to these properties, donkey's milk is a high-added value product, and, as such, it is subjected to adulteration with milk from other mammalian species, especially with cheaper cow's milk. This fraudulent practice results in an authenticity problem, but also in a real health issue. The proposed adulteration-detection study lays on these considerations and aims at developing a non-destructive approach for authenticating donkey's milk and for detecting its adulteration with cow's milk. To achieve this goal, Near Infrared (NIR) Spectroscopy was used to analyze 40 samples of genuine donkey's milk and 80 mixtures of donkey and cow's milk (at different ratios) to mimic the adulteration. Moreover, both pure and adulterated samples were subjected to successive freezing-thawing cycles and analyzed by NIR. To check the significance of this commonly used treatment, the data were handled by analysis of variance (ANOVA)-simultaneous component analysis (ASCA) [3]. Eventually, Partial Least Squares Discriminant Analysis (PLS-DA) was used to distinguish pure and adulterated donkey's milk samples, before and after freezing-thawing treatment. PLS-DA model on the untreated samples provided extremely good results in external validation, with the correct classification of all the test samples (100% accuracy). The PLS-DA approach achieved good accuracies also in the discrimination of freezed-thawed pure and adulterated milk samples (the correct classification rates were 85 and 100%, respectively), revealing that the effect of adulteration prevails on that of freezing-thawing, even though the latter was proved to be significant.

[1] K. Souroullas, M. Aspri, P. Papademas, *Food Res. Int.* **2018**, 109, 416–425.
[2] R. Derdak, S. Sakoui, O.L. Pop, C.I. Muresan, D.C. Vodnar, B. Addoum, R. Vulturar, A. Chis, R. Suharoschi, A. Soukri, B.E. Khalfi, *Foods*, **2020**, 9(9), 1302.
[3] J. J. Jansen, H. C. J. Hoefsloot, J. Van Der Greef, M. E. Timmerman, J. A. Westerhuis, A. K. Smilde, *J. Chemom.*, **2005**, 19(9), 469–481.

Connecting the dots between theory and practice: discovering new functional cocrystals through supervised pattern recognition

Fabio Fornari [a], Federica Bianchi [a, b], Marina Cocchi [c], Nicolò Riboni [a], Fabio Montisci [a], Paolo Pio Mazzeo [a, d], Claudia Carraro [a], Alessia Bacchi [a, d], Maria Careri [a, e]

[a] University of Parma, Department of Chemistry, Life Sciences and Environmental Sustainability, Parco Area delle Scienze 17/A, Parma, Italy; [b] University of Parma, Interdepartmental Center for Packaging (CIPACK), Parco Area delle Scienze, Parma, Italy; [c] University of Modena and Reggio Emilia, Department of Chemical and Geological Sciences, Via Giuseppe Campi 103, Modena, Italy; [d] University of Parma, Biopharmanet-TEC, Parco Area delle Scienze 27/A, Parma, Italy; [e] University of Parma, Interdepartmental Center on Safety, Technologies, and Agri-Food Innovation (SITEIA.PARMA), Parco Area delle Scienze, Parma, Italy

Essential oils (EOs) are complex mixtures of chemically diverse compounds naturally produced by plants with well-known insecticidal, antibacterial and antioxidant properties [1]. Their active components are Generally Recognized as Safe (GRAS) by the Food and Drug Administration [2], and they could offer more sustainable solutions than synthetic chemicals in many fields.

Cocrystallization [3] is a valuable crystal engineering approach for stabilizing highly volatile compounds into the solid state, allowing for the combination of one single active molecule with an array of partner molecules, leading to a palette of crystalline solids with improved properties without the need of any synthetic modification. Despite the great advantages offered by cocrystallization, it must be considered that not all the combinations of partner molecules, called coformers, end in forming cocrystals [4]. Therefore, the discovery of new cocrystals requires a great effort in terms of selection of coformers, synthesis and characterization.

In the frame of a research activity dealing with the synthesis of functional cocrystals based on EOs active compounds and other GRAS molecules to extend their use in different fields of application [5, 6], a chemometric approach is proposed to predict cocrystal formation. A Quantitative Structure–Property Relationship-like model based on Partial Least Squares–Discriminant Analysis served as a conjunction between the information encoded in a set of molecular descriptors and the outcomes of failed and successful cocrystallization experiments. Along with a correct classification rate on an external test set of 84%, the proposed methodology offers maximum flexibility and enables the researcher to gather data useful for the discovery of new cocrystalline materials at minimum experimental costs.

[1] F. Bakkali, S. Averbeck, D. Averbeck, M. Idaomar, *Food Chem. Toxicol.* **2008**, *46*, 446–475
[2] Food and Drug Administration **2016**, *81*, 54960–55055
[3] J.W. Steed, *Trends Pharmacol. Sci.* **2013**, *34*, 185–193
[4] M. D. Perera, J. Desper, A. S. Sinha, C. B. Aakeröy, *CrystEngComm* **2016**, *18*, 8631–8636
[5] F. Bianchi, F. Fornari, N. Riboni, C. Spadini, C. S. Cabassi, M. Iannarelli, C. Carraro, P.P. Mazzeo, A. Bacchi, S. Orlandini, S. Furlanetto, M. Careri, *Food Chem.* **2021**, *347*, 129051
[6] P.P. Mazzeo, C. Carraro, A. Monica, D. Capucci, P. Pelagatti, F. Bianchi, S. Agazzi, M. Careri, A. Raio, M. Carta, F. Menicucci, M. Belli, M. Michelozzi, A. Bacchi, *ACS Sustain. Chem. Eng.* **2019**, *7*, 17929–17940

SOMEnv: an R package for mining environmental monitoring datasets by Self-Organizing Map and k-means algorithms with a Graphical User Interface

Sabina Licen[a], *Marco Franzon*[b], *Tommaso Rodani*[c], *Sergio Cozzutto*[d], *Pierluigi Barbieri*[a]

[a] *Dept. of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1,34127 Trieste, Italy;* [b] *eXact lab s.r.l. , via Beirut, 2 - 34151 Trieste (Italy);* [c] *AREA Science Park - Padriciano, 99 34149 Trieste, Italy;* [d] *ARCO SolutionS s.r.l., spin-off company of the Dept. of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127 Trieste , Italy*

The Self-Organizing Map (SOM) algorithm [1] belongs to the family of artificial neural networks. It is an unsupervised method, so that no a prori knowledge about experimental data classification is needed. It can deal with large datasets and non-linear problems with powerful visualization features for outcome exploration on 2D maps [2]. For environmental pollution assessment other unsupervised techniques are widely used, e.g. principal component analysis and hierarchical cluster analysis [3]. However, their application for mining large datasets and properly visualizing the results is limited, especially considering that nowadays a variety of sensors recording high frequency data are available for environmental monitoring [4]. Thus, users are often forced to compact recorded data at every minute/few minutes to hourly or daily means in order to handle the data using the selected chemometric technique. This compaction process leads to a loss of information on the variability of the investigated environment.

Although the SOM algorithm may be a useful technique for handling the aforementioned data, it is not widely applied. It is possible that three combined concerns hamper the dissemination of this technique for environmental pollution assessments: (i) initialization parameter selection can be challenging for non-expert users; (ii) several available software tools require the user to have substantial experience in coding; and (iii) the outcome visualization tailored for high frequency recorded data is not straightforward.

This study presents an R package (SOMEnv) developed to allow non-expert users to elaborate by SOM algorithm environmental data recorded with high frequency for a rather long monitoring period. Additionally it can also be used for elaborating small dataset derived from uneven sampling. All the calculations and outcome visualizations can be done using the Graphical User Interface (GUI) so that experience in R software coding is not needed. A basic knowledge about the algorithm used is needed to interpret the results. The benefits of SOMEnv package are that (i) both the software environment and the tool are freely available; (ii) it is able to handle large dataset; (iii) it provides heuristic rules for SOM initialization [5]; (iv) it has a built-in GUI for performing calculations and (v) a wide range of visualizations with several of them dedicated to high frequency data monitoring. We propose an application example to optical particle counter data recorded near residential buildings close to an industrial plant at two different sites [6,7]. The package is freely available on the Comprehensive R Archive Network (CRAN) repository [8].

[1] T. Kohonen, *Appl. Opt.*, **1987**, 26, 4910.
[2] J. Vesanto, *Intell. Data Anal.*, **1999**, 3, 111–126.
[3] M. F. Dupont, A. Elbourne, D. Cozzolino, et al., *Anal. Methods*, **2020**, 12, 4597–4620.
[4] J. Chapman, V. K. Truong, A. Elbourne, et al., *Chem. Rev.*, **2020**, 120, 6048–6069.
[5] J. Vesanto and E. Alhoniemi, *IEEE Trans. Neural Networks*, **2000**, 11, 586–600.
[6] S. Licen, G. Barbieri, S. Cozzutto, M. Crosera, G. Adami and P. Barbieri, **2019,** *Data Br.*, 25
[7] S. Licen, S. Cozzutto, G. Barbieri, M. Crosera, G. Adami and P. Barbieri, *Chemom. Intell. Lab. Syst.*, **2019**, 190, 48–54.
[8] S. Licen, M. Franzon, T. Rodani, P. Barbieri, *Microchem. J.* **2021,** 165

Optode & Chemometrics: Milk Freshness at a Glance

Lisa Rita Magnaghi [a,b], Susanna Compagnin [a], Camilla Zanoni [a], Giancarla Alberti [a], Paolo Quadrelli [a,b] and Raffaela Biesuz [a,b]

[a] Dipartimento di Chimica, Università di Pavia, via Taramelli 12, 27100 Pavia, Italy;
[b] Unità di Ricerca di Pavia, INSTM, Via G. Giusti 9, 50121-Firenze, Italy

Milk plays a key role in human nutrition, being a complete food with high nutritional value, but, for the same reason, it is also an excellent growth medium for microorganisms. As a consequence, it is extremely perishable, and possesses a short shelf life. [1] The term "shelf life" refers to the time duration in which milk exhibits no physical and chemical changes. The "shelf life" is calculated in standard storage conditions and expressed through "best before" or "used by" dates. These dates are fixed by law and are intrinsically inaccurate; they do not account for better or worse storage conditions or innovative solutions that ensure elongation in milk shelf life.

Nowadays, conventional methods, usually destructive and time-consuming, are used to detect milk level of freshness in the dairy industry. Once in the supermarket or the household, milk freshness could no longer be controlled due to the lack of rapid, low-cost and reliable methods. [1]

To solve this issue, we developed a miniaturized colorimetric sensor, able to change colour according to milk freshness, following pH modifications provoked by microbial activity. After a preliminary investigation [2], we selected the suitable pH indicator. We covalently bound this receptor to EVOH copolymer. We obtained the final sensing unit, following the already presented procedure [3], shown in Figure 1a. The device was deeply tested on the whole and semi-skimmed fresh milk. Despite the apparent simplicity, this sensor gives reliable information, and it can be analysed at different levels.

Firstly, when milk is no longer eatable, a glaring colour shift from green to yellow can be clearly detected by the naked eye, as shown in Figure 1b. Secondly, the sensor colour evolution during milk storage, expressed as average RGB triplets, was used to develop classification models using Linear Discriminant Analysis (LDA) to predict the freshness of milk samples at any time. Eventually, sensor colour can be used to calculate milk acidity, expressed as °SH/100 mL, using Partial Least Square regression (PLS), as shown in Figure 1c.

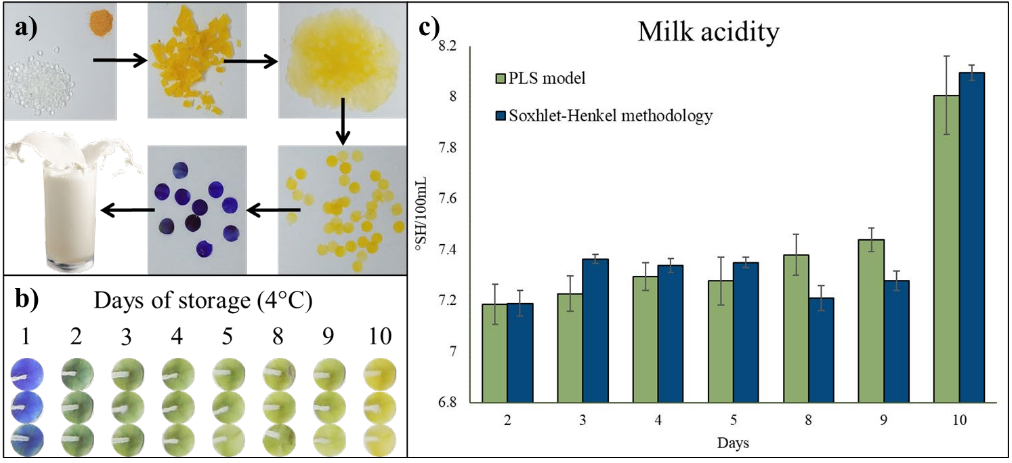


Figure 1: Miniaturised sensor preparation (a). Colour evolution during fresh milk storage in a domestic fridge (b). Comparison between milk acidity predicted by PLS model and measured by Soxhlet-Henkel methodology (c).

[1] M. Ziyaina, B. Rasco, S.S. Sablani, *Food Contr*. **2020**, *110*, 107008.
[2] L.R. Magnaghi et al., *ACS Food Sci. Technol.* **2021** in press
[3] L.R. Magnaghi et al., *ACS Food Sci. Technol.* **2021**, *1(2)*, 165-175

Optimization of the process of anaerobic digestion of FORSU by experimental design techniques

Elisa Robotti[a], Francesca Demichelis[b], Fabio Deorsola[b], Emilio Marengo[a]

[a] Department of Sciences and Technological Innovation, University of Piemonte Orientale, Viale Michel 11, 15121 Alessandria, Italy; [b] Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino (TO), Italy
e-mail: elisa.robotti@uniupo.it

In the last years many efforts have been spent to identify strategies for the exploitation of wastes for producing energy. In this framework, we present here a work which is part of the results obtained within the BIOENPRO4TO project (POR-FESR 2014-2020 - Regione Piemonte) aimed to the valorization of the Bioenergy and Bioproducts, starting from the integrated conversion processes of the organic fraction of municipal solid waste (FORSU), of primary and / or residual biomass and from other residuals that are generated by the daily life of the territorial communities of Turin Ovest and neighbouring. The work here presented deals with the optimization of the process of anaerobic digestion of FORSU by means of experimental design techniques. Anaerobic digestion was coupled to physical and biological pre-treatment strategies (mechanical, thermal, ultrasound, cavitation, enzymatic) to identify the best strategy for the production of biogas. In the case of pre-treatment by cavitation and ultrasound, the pre-treatment conditions were optimized separately from the digestion step, while for the other treatments, the pre-treatment and the anaerobic digestion were studied together, to identify also possible interactions between the first and the second step. Three factors were studied for what regards anaerobic digestion, i.e. the origin of the inoculation, the ratio between substrate (FORSU) and inoculum, and the incubation time. The origin of the inoculum is a qualitative parameter: two different types of inoculum were studied, i.e. mesophilic digestate of sewage sludge (WAS) and mesophilic digestate from livestock manure (CAS).

For what regards instead the pre-treatments, the parameters undergoing optimization were:

- Mechanical treatment: time of treatment;
- Thermal treatment: time of treatment and temperature;
- Enzymatic: type of enzyme, dose of enzyme.

Continuous experimental design techniques (full and fractional factorial designs, eventually with the addition of the star design) were exploited to identify the best set of experiments to identify the best technological conditions for running the process. The experiments were evaluated for what regards the specific biogas production, the lag phase and the process time. Desirability functions were also exploited to provide a general optimization taking into account all the three experimental responses contemporarily.

A chemometric strategy to exploit the complementary information from a combined XRF-Vis-NIR hyperspectral imaging system

Giorgia Sciutto[a], Emilio Catelli[a], Silvia Prati[a], Rocco Mazzeo[a], Michele Occhipinti[b], Roberto Alberti[b], Alessandro Tocchio[b], Tommaso Frizzi[b], Paolo Oliveri[c]

[a] Department of Chemistry "G. Ciamician", University of Bologna, Via Guaccimanni, 42 – 48121, Ravenna, Italy; [b] XGLab srl - Bruker Nano Analytics, via Conte Rosso 33, Milano, Italy; [c] Department of Pharmacy (DIFAR), University of Genova, Viale Cembrano, 4 – 16148 Genova, Italy

Hyperspectral imaging (HSI) systems that operate in different spectral ranges proved to be technologies highly potential to characterise, study and preserve cultural heritage objects, which typically present heterogeneous and complex surfaces.

However, due to the complexity of combined spectral imaging data, typically arranged as fused 3D arrays, advanced data processing strategies are usually required. This has often hindered the use of these technologies to non-research practitioners, excluding their implementation from the more conventional procedures and practices. In the few cases in which HSI techniques are applied, data processing is often performed in a univariate way and, therefore, the information is underutilised and results are quite limited.

To overcome these drawbacks, new simple and effective data processing methods are needed to combine different 3D datasets, from different spectral ranges, and to extract useful information from such complex matrices.

Within this scenario, the present research is aimed at developing an efficient multivariate strategy based on the combination between principal component analysis (PCA) and correlation diagrams (within and between spectral blocks) on the fused 3D datasets obtained with IRIS, a new cutting-edge instrument developed by Bruker Nano Analytics in the framework of the "MOBARTECH" project. This HSI system permits to acquire simultaneously, and with a single measurement head, spectral imaging data exploiting three different techniques: X-ray fluorescence (XRF, 1-40 keV), visible near infrared (VISNIR, 380–1100 nm) and short-wave infrared spectroscopy (SWIR, 1100–2500 nm). The data from the three techniques are co-registered, thus inherently saved with high space coherence, reducing the time for post-processing and correlated analysis. A complementary elemental and molecular characterisation is, therefore, provided simultaneously by this powerful analytical platform.

The chemometric strategy and the dedicated software developed proved to be highly efficient in data reduction and for the extraction of the most useful information coming from the three different spectroscopies, through an effective data visualisation and inter-correlation assessment.

Acknowledgments

This research was funded by Regione Lombardia Lombardia (POR FESR 2014 – 2020) in the framework of the Project "MOBARTECH: una piattaforma mobile tecnologica, interattiva e partecipata per lo studio, la conservazione e la valorizzazione di beni storico-artistici". Call Accordi per la Ricerca e l'Innovazione.

'Specialty' or 'Gourmet' oils: a multivariate statistical approach for the rapid identification of their botanical species

Federica Turrini[a], *Paola Zunin*[a], *Raffaella Boggia*[a]

[a] *Department of Pharmacy, University of Genoa, Viale Cembrano 4, 16148 Genoa, Italy;*

In the last decade, the increase of consumers' preferences for the pleasant sensorial features of oils of different botanical origin has favored the diffusion of the so-called 'specialty' or 'gourmet' oils, namely cold-pressed industrial virgin oils obtained from seeds, fruits, and nuts[1]. Besides their flavor and aroma, the peculiar features of 'gourmet' oils lay in their alleged health promoting activities[2], and in their low global production amounts, which result in their high costs. However, the recent market deregulation of virgin and/or cold pressed vegetable oils, and at the same time their high commercial value, asks for analytical methods which assess their authenticity. The aim of this study was evaluating the possibility to identify the botanical origin of the oil-based raw material by the routine analysis of their fatty acid composition coupled with chemometric methods and to explore also a new untargeted approach to their identification applying just their color analysis. A comprehensive data collection of authentic 'gourmet' oils, belonging to eight different botanical species (i.e., Almond, Apricot, Avocado, Hazelnut, Mosqueta rose, Rosehip, Sunflower, and Walnut) plus Olive oil as the gold standard of cold-pressed virgin oils, was performed. Their fatty acid composition has been re-elaborated in a statistical multivariate approach applying Principal Component Analysis (PCA) and classification methods. Moreover, a simple, rapid, and non-destructive spectrophotometric analysis has been considered to discriminate among different species. Particularly, the raw diffuse reflectance spectra recorded in the spectral range 380-780 nm by a UV-Vis spectrophotometer endowed with an integrating sphere was taken into account and elaborated by chemometrics. This information was compared with the results obtained by the most common approach based on the CIELab parameters and a fusion matrix of chromatographic and spectral data was also investigated. Both the fatty acid composition and the color (total spectrum and colorimetric parameters) of these vegetal oils have proven to be two promising markers of their botanical authenticity.

[1] N. Cicero, A. Albergamo, A. Salvo, G.D. Bua, G. Bartolomeo, V. Mangano, A. Rotondo, V. Di Stefano, G. Di Bella, G. Dugo, *Food Res. Int.* **2018**, 109, 517–525.

[2] E.M. Hernandez, *Functional Dietary Lipids—Food Formulation*. **2016**, 69–101.

Wearable electrochemical microneedles-based nanoporous gold sensor for real time catecholamine detection

C. Tortolini[a], M.A. Venneri[a], A.E.G. Cass[b], R. Antiochia[c]

[a]*Department of Experimental Medicine, Sapienza University of Rome, Rome, Italy*
[b]*Department of Chemistry & Institute of Biomedical Engineering, Imperial College, London, UK*
[c]*Department of Chemistry and Drug Technologies, Sapienza University of Rome, Rome, Italy*

Microneedle arrays for minimally invasive continuous sensing in the dermal interstitial fluid (ISF) have been demonstrated in both amperometric [1,2] and potentiometric [3] modes for detection of several biomarkers of clinical interest [4], however there are no publication where microneedle arrays have been used for direct monitoring of total catecholamines in ISF.

Dopamine, epinephrine and norepinephrine are the main catecholamine of clinical interest, as they play crucial roles in the regulation of nervous and cardiovascular systems and are involved in some brain behaviors, such as stress, panic, anxiety and depression. Changes of catecholamine concentrations in organisms have a close connection with some neurological disorders and certain diseases. Therefore, there is an urgent need for a reliable sensing device able to provide their continuous monitoring in a minimally invasive manner [4].

In this work, we present the first highly nanoporous gold (h-nPG) microneedles-based sensor for minimally invasive monitoring of catecholamine in ISF.

The highly nanoporous microneedles-based gold electrode was prepared by a simple electrochemical self-templating method that involves two steps, gold electrodeposition and hydrogen bubbling at the electrode, which were realized by sweeping the potential between +0.8 V and 0 V vs Ag/AgCl for 25 scans in a 10 mM $HAuCl_4$ solution containing 2.5 M NH_4Cl, and successively applying a fixed potential of -3 V vs. Ag/AgCl for 60 s [5]. The resulting microneedles-based h-nPG sensor displays an interference-free catecholamine detection without compromising its sensitivity, stability and response time.

The performance of the h-nPG microneedle array sensor for catecholamine detection was successively assessed in a hydrogel skin model at typical physiological concentrations.

[1] A.E.G. Cass, S. Sharma, *Meth. Enzymol.*, **2017**, *589*, 413.
[2] L. Ventrelli, L.M. Strambini, G. Barillaro, *adv. Healthcare Mater*., **2015,** *4*, 2606.
[3] T.M. Rawson, S. Sharma, P. Georgiou, A. Holmes, A.E.G. Cass, D. O'Hare, *Electrochem. Comm.*, **2017**, *82*, 1.
[4] J.A. Ribeiro, P.M.V. Fernandez, C.M. Pereira, F. Silva, *Talanta*, **2016,** 160, 653.
[5] P. Bollella, S. Sharma, A.E.G. Cass, F. Tasca, R. Antiochia, *Catalysts, **2019**, 9*, 580.

Solid state electrochemical behaviour and spin multiplicity in charge transfer co-crystals of DBTTF:F4TCNQ

Paolo Inaudi [a], *Federica Solano* [b], *Mario Chiesa* [c], *Enrico Salvadori* [c], *Ornella Abollino* [a],

Enrico Da Como [d], *Mery Malandrino* [c], *Claudio Fontanesi* [e], *Agnese Giacomino* [a]

[a] *Department of Drug Science and Technology, University of Torino, Via Pietro Giuria 9, Torino 10125, Italy;*
[b] *Dep ens sciences Chimie - Recherche Dép Chimie , Université Angers, 2 Boulevard de Lavoisier - 49045 - Angers*
[c] *Department of Chemistry, University of Torino, Via Pietro Giuria 5, Torino, 10125, Italy*
[d] *Centre for Photonics and Photonic Materials, Department of Physics, University of Bath, BA2 7AY, United Kingdom*
[e] *DIEF, University of Modena e Reggio Emilia, Via Vivarelli, 10- 41125 Modena, Italy*

Charge-transfer crystals (CTCCs) exhibit unique electronic and magnetic properties with interesting applications. CTCCs synthesis is based on their different electronic affinity, on the difference between the ionization potentials and for mutual polarization [1]. The charge-transfer single crystal formed by dibenzotetrathiafulvalene (DBTTF) together with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) presents a long-range ordered supramolecular structure of segregated stacks, with a unitary degree of charge transfer. Thus, the crystal structure is composed of dimerized radical molecules with unpaired electrons. The energy levels and the spin degrees of freedom of this material were investigated by solid-state electrochemistry and electron paramagnetic resonance (EPR) spectroscopy [2]. The electrochemical data, supported by density functional theory calculations, show how this organic Mott insulator has an electronic gap in the range of hundreds of meV. EPR experiments show the presence of a ground-state $S = 1$ triplet spin state along with localized $S = 1/2$ spins. The calculations also predict a ground-state triplet configuration, with the singlet configuration at 170 meV higher energy. DBTTF/F4TCNQ seems to be a candidate material for organic electronic and spintronic applications.

[1] O. Kataeva, M. Khrizanforov, Y. Budnikova, D. Islamov, T. Burganov, A. Vandyukov, K. Lyssenko, B. Mahns, M. Nohr, S. Hampel, M. Knupfel, Cryst. Growth Des., **2016**, 16, 331–338.
[2] F. Solano, P. Inaudi, M. Chiesa, G. Kociok-Köhn, E. Salvadori, E. Da Como, D. Vanossi, M. Malandrino, R. Carmieli, A. Giacomino, C. Fontanesi, J. Phys. Chem. C, **2021,** 125, 8677–8683.

Large-scale production of electroanalytical sensors by combined inkjet printing and light-induced synthesis of metal nanoparticles

Andreas Lesch, Domenica Tonelli

University of Bologna, Department of Industrial Chemistry "Toso Montanari", Viale del Risorgimento 4, 40136 Bologna, Italy

Since decades, disposable electroanalytical sensors based on graphite and other carbonaceous materials, such as graphene and carbon nanotubes, are successfully fabricated by using screen printing. A wide range of conductive and dielectric pastes, as well as, screen-printers can be purchased and operated at relatively low cost. The working electrodes can be further functionalized, for instance by depositing metal-based, catalytically active nanoparticles and composites, to improve the sensitivity and selectivity for sensing applications. Nevertheless, screen printing becomes disadvantageous for research purposes when low and limited quantities of new electrode materials are under study. In most cases, drop casting is carried out with limited accuracy and reproducibility. Recently, mask-less material deposition techniques based on drop-on-demand ink delivery systems, such as inkjet printing, have come increasingly into focus. The number of commercially available metal nanoparticle-based inkjet inks with improved stability and extended shelf life increases constantly. The transfer of an inkjet printing process from a small lab-scale inkjet printer to large-scale industrial platforms is becoming very efficient and attractive, as leading printing companies nowadays use the same printhead technology in differently scaled printing platforms. Inkjet inks must fulfill certain physicochemical properties, in particular viscosity and surface tension, but nanoparticle-based inks can suffer in addition from the agglomeration and precipitation of the nanoparticles leading to rapid and irreversible blocking of the printhead nozzles. An alternative to the sequential steps of nanoparticle synthesis, formulation of stable inks and development of the inkjet printing process, consists in the *in situ* synthesis of metal nanoparticles by simultaneous inkjet printing and high intensity light irradiation of easily jettable inks that contain dissolved metal precursor compounds. We named this process Print-Light-Synthesis, which can be used to produce single and mixed metal nanoparticles and nanostructures [1-2].

In this presentation, the focus will be made on inkjet printing in combination with high intensity light irradiation, in particular using UV, for the large-scale production of electrochemical sensors. The process is based on the micrometrically resolved deposition of metal precursor ink droplets and their immediate conversion into metal nanoparticles by light-induced redox chemistry. The conversion of the precursors is based on both photochemical and thermal processes, which are highly controllable by the ink composition as well as by the parameters related to inkjet printing and light irradiation. Examples will especially include flexible platinum- and gold-nanoparticle-coated graphene electrodes. The successful application of the inkjet-printed sensors will be demonstrated for the detection of biomolecules as markers for bacterial infections in blood and wound fluids [3-5].

[1] A. Lesch, *Adv. Mater. Technol.* **2018**, *3*, 1700201.
[2] V. Costa Bassetto, M. Mensi, E. Oveisi, H. H. Girault, A. Lesch, *ACS Appl. Energy Mater.* **2019**, *2*, 6322−6331.
[3] Y. Zhu, M. Jović, A. Lesch, L. T. Lovey, M. Prudent, H. Pick, H. H. Girault, *Angew. Chem. Int. Ed.* **2018**, *57*, 14942-14946.
[4] R. Jarosova, S. E Mcclure, M. Gajda, M. Jović, H. H. Girault, A. Lesch, M. Maiden, C. Waters, G. M. Swain, *Anal. Chem.* **2019**, *91*, 8835-8844.
[5] B. Nagar, M. Jović, V. Costa Bassetto, Y. Zhu, H. Pick, P. Gómez-Romero, A. Merkoçi, H. H. Girault, A. Lesch, *ChemElectroChem* **2020**, *7*, 460–468.

Combined paper-based substrates for electrochemical detection of copper ions in serum

Antonella Miglione[1], *Stefano Cinti*[1,2*]

1 Department of Pharmacy, University of Naples "Federico II", Via D. Montesano 49, 80131 Naples, Italy.

2 BAT Center - Interuniversity Center for Studies on Bioinspired Agro-Environmental Technology, University of Napoli Federico II, 80055 Naples, Italy

Copper (Cu) is as an essential metal playing a crucial role in various biochemical reactions as a co-factor of many metalloenzymes and in physiological regulations. Although copper ions are mainly bound to serum proteins, from a clinical perspective the determination of copper in its unbound form is of particular interest because of its high toxicity [1]. Traditional analytical methods mainly adopted to determine copper levels in biological matrices, i.e. atomic absorption spectroscopy (AAS), ion coupled plasma-mass spectrometry (ICP-MS), have their major drawbacks due to the necessity of skilled personnel, sophisticated instruments and time-consuming procedures to obtain results. This is the reason why easy-to-use and portable methods are highly required, in particular to allow citizens to self-monitor their health. Among these, paper-based substrates represent a valuable choice towards this aim. In particular, the electroanalytical field has exploited great advantages in using paper-based substrates, even if the word "paper" might be general [2]. In fact, the mainly adopted paper-based substrates are often chromatographic and office ones. Chromatographic paper is well-established for storing reagents/treating samples, but the sensitivity compared to traditional screen-printed is lower (due to porosity), while office paper represents a sustainable alternative to plastic (with similar sensitivity) but its porosity is not enough to load reagents.

To overcome the limitations that might arise due to the adoption of a type of individual paper-based substrate, herein we describe for the first time, the development of a 2D merged paper-based devices for electrochemical copper ions detection in serum. In this work we report a novel configuration to produce an integrated all-in-one electrochemical device, in which no additional working media has to be added by the end user and the sensitivity can be tuned by rapid pre-concentration on porous paper, with the advantage of making the platform adaptable to real matrix scenario (Figure 1).

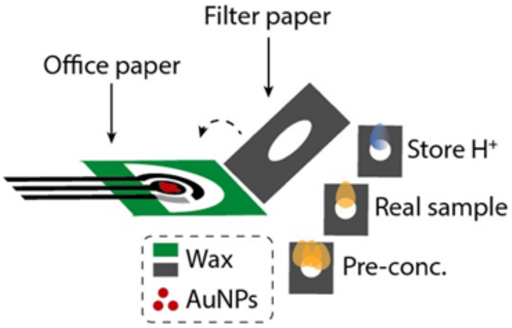


Figure 1. Architecture of the combined office/chromatographic paper-based device for copper sensing.

The novel architecture has been obtained by combining office paper to screen-print a sustainable and robust electrochemical strip, the printed electrochemical strips and chromatographic one to 1) store the reagents, 2) collect real sample and 3) pre-concentrate the analyte of interest. The novel sensing platform has allowed to obtain a detection limit for copper ions down to 5ppb in all the solutions that have been interrogated, namely standard solution and serum, and a repeatability of ca. 10% has been obtained.

[1] Letelier, M. E., Sánchez-Jofré, S., Peredo-Silva, L., Cortés-Troncoso, J., & Aracena-Parks, P., *Chemico-biological interactions*, **2010**, 188(1), 220-227.
[2] Cinti, S., Moscone, D., & Arduini, F., *Nature protocols,* **2019**, 14(8), 2437-2451.

Enantiomer discrimination in voltammetry in media of high structural order at the electrochemical interphase implemented with chirality

Patrizia Romana Mussini, Sara Grecchi, Serena Arnaboldi

Università degli Studi di Milano, Dipartimento di Chimica, Via Golgi 19, 20133 Milano

Discrimination of the enantiomers of electroactive chiral molecules in voltammetry is a fascinating frontier target. Of course the necessary condition to achieve it is that the two enantiomers undergo electron transfer in energetically different conditions. Since in an achiral context they would have identical physico chemical properties and thus also identical voltammetry features, this requires the implementation at the electrode|solution interphase of a suitable enantiopure chiral selector.

The so far most popular strategy consists in working on chiral electrode surfaces, and an impressive variety of approaches has been proposed [1,2]. However, working on achiral electrodes with chirality implemented in the medium has also been proposed [1,3], and very recent experiments have highlighted that this approach can yield outstanding discrimination in terms of potential differences for the enantiomers of chiral electroactive probes, when working in media of high structural order at the charged interphase, like ionic liquids ILs [3-7] and deep eutectic solvents DESs [8], implemented with chirality [5,6,9] or, even better, inherent chirality [4,7,8].

Such achievements will be comparatively presented and commented in terms of IL and DES structural order at the interphase (also compared to classical media and to ionic liquids / ionic liquid crystals [9]) as well as of possibility of probe/selector specific interactions.

Support to our chiral electroanalysis research line by Fondazione Cariplo/Regione Lombardia as well as by Università degli Studi di Milano is gratefully acknowledged.

[1] S. Arnaboldi, M. Magni, P.R. Mussini, *Curr. Opin. Electrochem.* **2018**, 8, 60-72. (minireview)

[2] S. Arnaboldi, M. Magni, S. Grecchi, P.R. Mussini, *Curr. Opin. Electrochem.* **2018**, 7, 188-189. (minireview)

[3] S. Grecchi, S. Arnaboldi, P.R. Mussini, *Curr. Opin. Electrochem.,* accepted May **2021**. (minireview)

[4] S. Rizzo, S. Arnaboldi, V. Mihali, R. Cirilli, A. Forni, A. Gennaro, A. A. Isse, M. Pierini, P. R. Mussini, F. Sannicolò, *Angew. Chem. Int. Ed.* **2017**, 56, 2079 –2082.

[5] M. Longhi, S. Arnaboldi, E. Husanu, S. Grecchi, I. F. Buzzi, R. Cirilli, S. Rizzo, C. Chiappe, P. R. Mussini, L. Guazzelli, *Electrochim. Acta* **2019**, 298, 194-209.

[6] S. Grecchi, C. Ferdeghini, M. Longhi, A. Mezzetta, L. Guazzelli, S. Khawthong, F. Arduini, C. Chiappe, A. Iuliano, P. R. Mussini, *ChemElectroChem* **2021**.

[7] S. Rizzo, S. Arnaboldi, R. Cirilli, A. Gennaro, A. A. Isse, F. Sannicolò, P. R. Mussini, *Electrochem. Commun*. **2018**, 89 57-61

[8] F. Fontana, G. Carminati, B. Bertolotti, P. R. Mussini, S. Arnaboldi, S. Grecchi, R. Cirilli, L. Micheli, S. Rizzo, *Molecules* **2021**, 26, 311-324.

[9] S. Arnaboldi, A. Mezzetta, S. Grecchi, M. Longhi, E. Emanuele, S. Rizzo, F. Arduini, L. Micheli, L. Guazzelli, P. R. Mussini, *Electrochim. Acta* 2021

Cannabinoids fast detection in real matrices: an electrochemical sensors' approach

Laura Pigani[a]*, Alessandro Monari*[a]*, Giorgia Foca*[b]*, Alessandro Ulrici*[b]*, Gabriele Bevini*[a]*, Barbara Zanfrognini*[c]*, Chiara Zanardi*[a,c]

[a] *Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via Campi 103, 41125 Modena, Italy;*
[b] *Department of Life Sciences, University of Modena and Reggio Emilia, via Amendola 2, 42122 Reggio Emilia, Italy;*
[c] *Institute of Organic Synthesis and Photoreactivity (ISOF), National Research Council of Italy (CNR), Via P. Gobetti 101, 40129 Bologna, Italy.*

Cannabinoids are terpenophenolic compounds of great interest which have been extensively investigated due to their important pharmacological properties. Phytocannabinoids are cannabinoids derived from *Cannabis sativa L*; among them, trans-Δ^9-tetraidrocannabinol (THC) is widely known for its psychoactivity while cannabidiol (CBD), which is non-psychoactive, is known for its neuroprotective, anti-inflammatory and analgesic characteristics. While recreational *Cannabis*, mainly marijuana and hashish, are illicit drugs possessing high levels of THC and low levels of CBD, many countries have recently legalized the use of fibre-type *Cannabis* and related products (oils, edibles and even dried plant parts).

Up to now the determination of cannabinoids in real samples and the quantification of THC/CBD ratio in compliance with countries regulations, is carried out by chromatographic techniques; however, the non-portable instrumentation, the reagent -consuming sample preparation and longtime analysis do not allow *in-situ* detection. Recently, electrochemical sensors have received considerable interest as possible alternatives to chromatographic techniques for a fast cannabinoid screening, thanks to their low cost, handiness and miniaturization possibility, allowing real-time control of target analytes [1]. THC and CBD, as well as their precursors present in the plant, cannabidiolic acid (CBDA), and Δ^9-tetrahydrocannabinolic acid (THCA) are electroactive due to the oxidation of the phenolic group, so they are good candidates for electrochemical analysis.

This work is focused on the development of sensors exploiting the electroactivity of cannabinoids to perform qualitative and quantitative analysis, even in real matrices extracts. In particular, among all the electrodic materials tested, screen printed electrodes (SPEs) modified with carbon black (CB) showed very promising results [2]. The sensors' ability to recognize samples containing the various cannabinoids has been explored, coupling voltammetric techniques to chemometric data analysis. The first experiments have been conducted in aqueous/methanol mixtures containing the target analytes; then measurements have been performed in aqueous/methanol extracts of *Cannabis* real samples (fibre-type *Cannabis*, "*Cannabis* light", recreational *Cannabis* and therapeutic *Cannabis*), characterised by different amounts of THC, THCA, CBD and CBDA. The electrochemical procedure proposed, together with the good detection performances of SPE-CB electrodes, leads to excellent results, suggesting the possibility to discriminate between the different samples of Cannabis performing a fast electrochemical measurement.

[1] B. Zanfrognini, L. Pigani, C. Zanardi, *J. Solid State Electrochem.* **2020**, *24*, 2603.
[2] M. Cirrincione, B. Zanfrognini, L. Pigani, M. Protti, L. Mercolini, C. Zanardi, *Analyst* **2021**, *146*, 612.

Electrochemical Characterization of supramolecular structure in Self-Assembled Monolayers

Tricase Angelo [a], Bollella Paolo [a], Macchia Eleonora [b], Torsi Luisa [a,b,c]

[a] Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", 70125 Bari (Italy); [b]The Faculty of Science and Engineering, Åbo Akademi University, 20500 Turku (Finland); [c]CSGI (Centre for Colloid and Surface Science), 70125 Bari (Italy).

Self-assembled monolayers (SAMs) were described for the first time at the early '90 [1], gaining an increasing interest in the last few years thanks to their implementation in different bioelectronic devices as surface plasmon resonance (SPR) and field-effect transistors (FETs) [2,3]. In particular, a peculiar and very promising application was reported in the gate electrode of biosensors based on electrolyte gated organic field-effect transistors (EGOFETs), able to reach the physical limit of sensitivity [4]. In similar devices SAMs are typically used to efficiently immobilize the biorecognition element [5], but Macchia et al. hypothesized also a role in improving device performance thanks to the formation of a diffuse hydrogen bonding network between chains [4].

For the analytical point of view, a deeper understanding of the supramolecular behaviour of the SAMs play a crucial role in studying similar devices, so Au substrates after SAM growing process were cycled in a buffered solution and periodically analysed in a separate cell using two different electrochemical approaches: cyclic voltammetry in $[Fe(CN)_6]^{4-}$ for evaluating kinetic of the ionic interpenetration/diffusion in the SAM structure, described using a mixed model based on Klingler-Kochi and Nicholson-Shain methods, and Electrochemical Impedence Spectroscopy (EIS) for analysing the equivalent circuit configuration. Moreover, differential pulse voltammetry (DPV) in $[Fe(CN)_6]^{4-}$ and $[Ru(NH_3)_6]^{2+}$ was used to evaluate the pK_a of the surface for pH-dependant SAM bearing carboxylic groups

These results were compared with well-known trend available for other SAM structures for correlating supramolecular behaviour of the SAM due to the electric field application with performance of EGOFETs biosensors.

[1] R.G. Nuzzo, L.H. Dubois, D.L. Allara, J. Am. Chem. Soc., **1990**, *112*, 558–569.
[2] K.V. Gobi, K. Matsumoto, K. Toko, H. Ikezaki, N. Miura, , Anal. Bioanal. Chem., **2007**, *387* 2727–2735
[3] S. Casalini, C.A. Bortolotti, F. Leonardi, F. Biscarini, Chem. Soc. Rev., **2017**, *46,* 40–71.
[4] E. Macchia, K. Manoli, B. Holzer, C. Di Franco, M. Ghittorelli, F. Torricelli, D. Alberga, G.F. Mangiatordi, G. Palazzo, G. Scamarcio, L. Torsi, Nat. Commun., **2018,** *9*
[5] F. Leonardi, A. Tamayo, S. Casalini, M. Mas-Torrent, RSC Adv., **2018**, *8*, 27509–27515.

Specific ion effect in electrochemistry: the deposition of copper in the presence of different background electrolytes.

Martina Vizza [a], *Alberto Fidi* [a], *Erasmo Anselmi* [a], *Walter Giurlani* [a,b], *Lorenzo Fei* [a], *Emiliano Carretti* [a], *Duccio Tatini* [a], *Pierandrea Lo Nostro* [a], *Massimo Innocenti* [a,b,c]

[a] *Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy;* [b] *National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy;* [c] *Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy.*

For a number of years, the specific ion (or Hofmeister) effect has been the subject of several studies of scientific and industrial interest, spanning from biochemical to inorganic, and from bulk solutions to interfacial systems [1]. These phenomena have been studied and reported since the end of the 19th century. However, to date there are only a few works in literature on Hofmeister effects in electrochemical applications. According to their specific effects, ions are attributed either a chaotropic or a kosmotropic nature. The series, that does depend on the particular experiment, ranks the ions according to their effectiveness, e.g. as:

$$\text{cirate}^{3-} > CO_3^{2-} > SO_4^{2-} > H_2PO_4^- > F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-$$

This work looks for a connection between the specific ion effect and the electrodeposition of transition metals, e.g. copper, from galvanic baths with a reduced environmental impact. Solutions without organic additives and surfactants were formulated. Electrolytes of various kinds were added, using saline species in which the same cation was kept constant while varying the anions, in relation to the Hofmeister series. The influence of the nature and type of anions on the efficiency and morphology of metal deposition was studied. Furthermore, the kinetics of plating was examined, varying the electrolyte concentration, keeping the temperature constant and considering other factors, such as the formation of bubbles near the electrode/solution interfacial zone due to the presence of dissolved gases. This study was sustained by electrochemical, morphological and crystalline characterization. Therefore, this work aims at opening up new perspectives in the field of electrodeposition, both from a scientific and technological point of view, able to provide green alternatives in the electroplating industry [2].

The authors acknowledge Regione Toscana POR CreO FESR 2014-2020 – azione 1.1.5 sub-azione a1 – Bando 1 "Progetti Strategici di ricerca e sviluppo", which made possible the "GIGA 4.0" (CUP 3553.04032020.158000105_1242).

[1] P. Lo Nostro, B. W. Ninham, *Chem. Rev.* **2012**, *112*, 2286-2322.
[2] W. Giurlani, G. Zangari, F. Gambinossi, M. Passaponti, E. Salvietti, F. Di Benedetto, S. Caporali, M. Innocenti, *Coatings* **2018**, *8*, 260.

POR CreO 2014 2020 REGIONE TOSCANA FONDO EUROPEO DI SVILUPPO REGIONALE
Unione Europea Fondo Europeo di Sviluppo Regionale
REPUBBLICA ITALIANA
Regione Toscana

Differentiation and profiling of Morocco species belonging to Lamiaceae Family by Ambient Mass Spectrometry methods

Domenica Mangraviti[a], *Francesca Rigano*[a], *Paola Dugo*[a,b,c,d]
Luigi Mondello [a,b,c,d]

[a]*Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b]*Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[c]*Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy;*
[d]*BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

Medicinal & Aromatic Plants (MAPs) are a valuable resource of functional compounds responsible of beneficial effects on human health and employed for therapeutic purposes in pharmaceutical field. On the other hand, as consequence of essential oils present in their extracts, aromatic plants are characterized by distinctive flavors useful in food preparation, and at industrial level for the production of beverages, cosmetics, and perfumes.

Such properties may explain the economic interest around them, and make MAPs susceptible to illegal practices, involving mislabeling, adulteration with less valuable botanical species or addition of not declared ingredients.

Although chromatographic methods coupled to mass spectrometry (MS) are commonly employed to investigate the phytochemical components of plants, belonging to a specific chemical class, the discovery of fraudulent activities is based on the use of fast fingerprinting techniques, such as direct-MS strategies coupled to chemometrics for the reliable identification of authentic species.

In the present study, six Moroccon species of Lamiaceae Family, originated from different pedo-climatic areas (*Mentha pulegium, Mentha suaveolens*, *Melissa officinalis, Calamintha nepeta*, *Thymus zigis, Sideritis incana*), were analyzed by distinct ambient MS (AMS) approaches, namely Rapid Evaporative Ionization Mass Spectrometry (REIMS) and Direct Analysis in Real Time (DART), for the screening of the total metabolome. No relevant sample preparation procedures were required for the two methods and ionization processes occured directly on raw material under atmospheric conditions.

REIMS and DART techniques led to obtain almost instantaneously unique fingerprinting of the samples of interest revealing the presence of marker compounds and discriminant features. Moreover, classification models based on statistical analysis were employed for the differentiation of the botanical species. The comparison between the mass spectra profiles and statistical models of both AMS strategies revealed their ability to be applied for the reliable identification of aromatic plants and consequently as valid tools against fraud activities.

Advancements in Direct-MS using SPME coupled to Liquid-EI and CI

Nicole Marittimo,[a] Giorgio Famiglini,[a] Pierangela Palma,[a] Achille Cappiello[a]

[a]LC-MS Laboratory, Department of Pure and Applied Sciences, University of Urbino, Piazza Rinascimento 6, Urbino, Italy. E-mail: nicole.marittimo@campus.uniurb.it

There is a growing interest in the development of simple technologies that can combine the sampling and sample preparation steps with direct introduction to Mass Spectrometry (MS).[1] Solid-Phase Microextraction (SPME), directly coupled to MS, has become an effective means for the quantitative determination of a broad range of compounds in different matrices in a wide variety of application fields.[2] In this context, we have recently developed a modified microfluidic open interface connected to a passive flow splitter (MOI-PS) for the coupling of SPME to a liquid electron ionization-tandem mass spectrometry (LEI-MS/MS) system and then to a liquid chemical ionization-tandem mass spectrometry (LCI-MS/MS) system for the direct analysis, avoiding sample cleanup and chromatographic separations, of complex biological and environmental samples. In the first case, we selected fentanyl as model compound. The analytical workflow consists of the direct immersion of a C18 Bio-SPME fiber into plasma within a short period of time (3 min.) followed by a quick desorption step (1 min.) in a flow-isolated volume (2.5μL) filled with acetonitrile. Rapidly flowing at microliters per minute, by means of a passive splitter, a fraction of the sample is then transferred to an EI source of a triple quadrupole mass spectrometer via a LEI interface at nano scale flow rate (LEI works only at nano flow rates). In the second case, the same setup has been applied for the detection of tefluthrin in water samples using negative chemical ionization (NCI) with methane as reagent gas. Altogether, the sampling, desorption and analysis procedure requires less than 5 min. With fentanyl and tefluthrin, quantitation at microgram and nanogram per liter levels was obtained, respectively. The MOI-PS device is suitable for the hyphenation of SPME fibers with different ionization sources, in fact, the design was successfully applied to both EI and CI sources. The method workflow is simple, fast, sustainable, and leads to reproducible results.

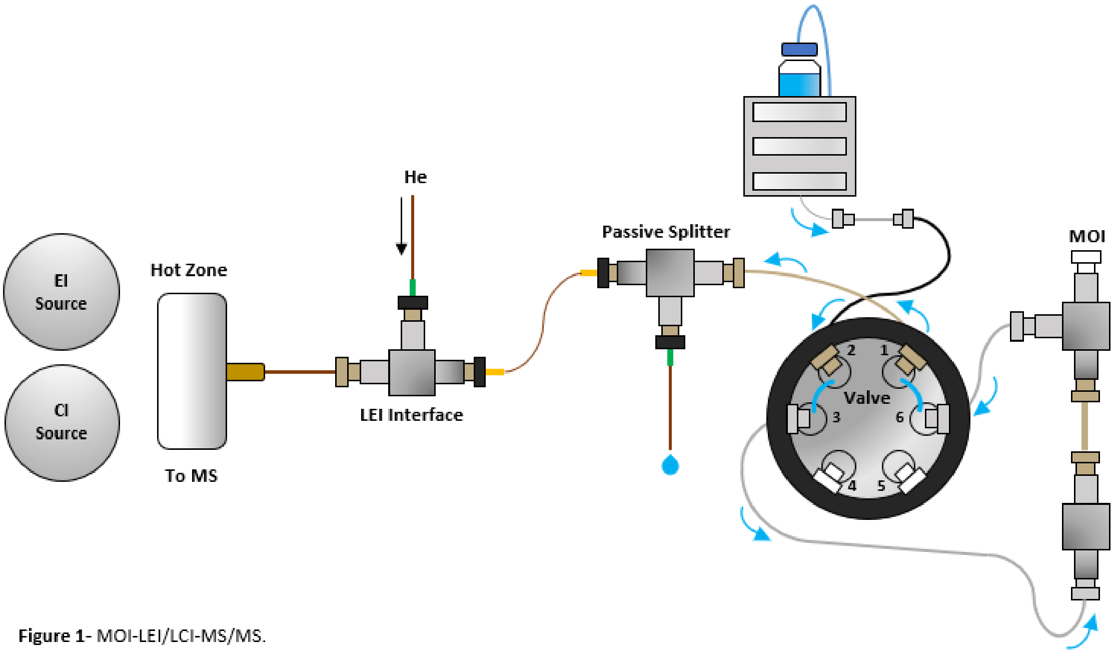


Figure 1- MOI-LEI/LCI-MS/MS.

[1] M. Tascon, M. N. Alam, G. A. Gomez-Rios, J. Pawliszyn, *Anal. Chem.* **2018**, 90, 2631.
[2] P. Rocío-Bautista, G. Famiglini, V. Termopoli, P. Palma, E. Nazdrajić, J. Pawliszyn, A. Cappiello, *J. Am. Soc. Mass Spectrom.* **2021**, 32, 262.

Characterization of bioactive compounds from natural products using focusing-modulated comprehensive two-dimensional liquid chromatography coupled to mass spectrometry

Katia Arena[a], *Francesco Cacciola*[b], *Paola Dugo*[a,c], *Luigi Mondello*[a,c,d,e]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, 98168, Ital;* [b] *Department of Biomedical, Dental, Morphological and Functional Imaging Sciences, University of Messina, Messina, 98125, Italy;* [c] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, 98168, Italy;* [d] *Department of Sciences and Technologies for Human and Environment, University Campus Bio-Medico of Rome, Rome, 00128, Italy;* [e] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, 98168, Italy.*

Comprehensive two-dimensional liquid chromatography is a well-established method for the unraveling of complex real-world samples. With regard to food and natural products such a technique turned out to be a very promising approach due to its high resolving power and improved identification capability, especially in combination with mass spectrometry. In this context, polyphenols comprise a complex class of bioactive compounds, due to their nature and high content in commonly consumed foodstuffs, making their analysis challenging. The present contribution highlights the benefits of the novel approach used for polyphenol analysis, *viz.* HILIC×RP-LC in conjunction with the focusing modulation approach.

The latter clearly allowed the attainment of higher resolving power and peak capacity compared to non-focusing modulation set-ups. Moreover, the use of active modulation by the addition of a make-up flow efficiently helped to compensate for the solvent strength mismatch produced between the two dimensions.

In this contribution the developed HILIC×RP-LC method showed a good separation of secondary metabolites allowing an improvement of practical peak capacity and orthogonality with respect to the available methodologies for the analysis of complex food samples such as berry juices and sumac fruits.

In addition, a quantification approach was carried out through different standards and the calibration curves were created automatically by the use of Chromsquare software and the method was validated yielding satisfactory LODs and LOQs values.

Furthermore, the polyphenols characterization of these samples will aid to confirm their potential contribution to human health.

Analysis of phenolic compounds in plant matrices by means of HPLC-MS/MS with targeted and semi-untargeted approach

[a]Eleonora Oliva, [a]Federico Fanti, [a]Sara Palmieri, [a]Eduardo Viteritti, [a]Fabiola Eugelio, [a]Alessia Pepe, [a]Manuel Sergi, [a]Dario Compagnone

[a]*University of Teramo, Faculty of Bioscience and Technology for Food, Agriculture and Environment, Teramo, Italy.*

Polyphenols (PC) are natural secondary metabolites of plants, in which they have a significant physiological and morphological importance and perform various biological functions. They have been extensively studied for their potential in the prevention and treatment of diseases related to oxidative stress, such as metabolic disorders, cancer, diabetes and cardiovascular disease, as they can prevent the oxidative damage of biomolecules (DNA, lipids and proteins), induced by reactive oxygen species [1].

There are numerous analytical approaches used for the determination of PCs in plants, but liquid chromatography (LC) is certainly the most used, generally coupled to different detectors, such as UV-vis, DAD and MS. With LC-MS it is possible to work either in targeted mode [2], generally coupled to low resolution MS (LRMS), usually triple quadrupole (QqQ), or in untargeted mode, usually with high resolution MS (HRMS) [3].

In this work, two different approaches, one targeted and one semi targeted, were evaluated for the quantification and/or putative identification of phenolic compounds (PCs) in plant matrices by HPLC-MS/MS. With the targeted approach, based on the MRM acquisition mode, it was possible to identify and quantify a list of target analytes with respect to the standards; in the second approach, a semi targeted analysis, by means of precursor and neutral loss ion scans was used for the tentative identification of compounds not included in the target list.

The analysis was performed on three different plant matrices (curry leaves, hemp and blueberry). To minimize the presence of interfering compounds, an extraction and purification method was also developed, which allowed to obtain a low matrix effect (>16%) and reliable recovery values (from 45% 98%) for all analytes.

The approach allowed to obtain a sensitive and robust quantitative analysis of the target compounds with LOQ between (0.0002 and 0.05 ng mg-1), which allowed the identification and quantification, in all three matrices, of various hydroxycinnamic and hydroxybenzoic acids, as well as numerous flavonoids.

To extend the characterization of the matrices under consideration, different fractions such as neutral losses or precursor ions were evaluated in the semi targeted MS/MS approach, which allowed an putative identification of different glycosylated forms of flavonoids, such as luteolin-galactoside and diosmin all three matrices, while apigenin-glucuronide was detected in hemp and quercetin-glucuronide in blueberry.

A further study with MS^3, by activation a further fragmentation in the linear ion trap (LIT), was conducted to discriminate compounds with similar aglycones, such as luteolin and kaempferol.

[1] P.K. Mukherjee, Polyphenols and Human Health: A Prospectus, Food Science and Nutrition, *Rev.* **2011**, *51, 524-546.*

[2] M.J. Motilva, A. Serra, A. Macià, Analysis of food polyphenols by ultra high-performance liquid chromatography coupled to mass spectrometry, J. Chromatogr. A, *Rev.* **2013**, *1292, 66–82.*

[3] O. López-fernández, R. Domínguez, M. Pateiro, P.E.S. Munekata, G. Rocchetti, J.M. Lorenzo, Determination of polyphenols using liquid chromatography–tandem mass spectrometry technique (LC–MS/MS), Antioxidants, *Rev.* **2020**, *1–27.*

The Coupling of Gas Chromatography - Mass Spectrometry with Infrared Spectroscopy for Reliable Identification of Unknowns in Complex Samples

Tania M. G. Salerno,[a] *Carmelo Coppolino,*[b] *Mariosimone Zoccali,*[c] *Paola Donato,*[d] *Luigi Mondello*[a,b,e]

[a] *BeSep S.r.l. c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[c] *Department of Mathematical and Computer Science, Physical Sciences and Earth Sciences, University of Messina, Messina, Italy*
[d] *Department of Biomedical, Dental, Morphological and Functional Imaging Sciences, University of Messina, Messina, Italy*
[e] *Chromaleont S.r.l. c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

A new hyphenated instrument consisting of a gas chromatograph (GC) coupled to mass spectrometry (MS) and solid deposition Fourier Transform Infrared Spectroscopy (*sd*-FTIR) will be illustrated. The hardware coupling of GC-MS with FTIR was achieved by means of an external heated transfer-line developed in our laboratory. In this novel configuration, the exiting GC column flow was diverted to the two detectors by using capillaries of different length and size, to adjust the flow ratio, in order to meet the sensitivity requirements of both the detectors. Furthermore, the use of the solid state interface, compared to a gas phase (light pipe) one, enabled to overcome the limitations related to the rather poor detection limits of GC-FTIR technique. [1] The complementary information, achieved by the parallel detection, and in addition, the use of Linear Retention Indices (LRI) strongly reduced the possibility of a misidentification. The results obtained demonstrated the effectiveness of the hyphenated instrument, in providing a single automated technique, for the identification of unknowns.

The authors gratefully acknowledge Shimadzu Corporation and Merck Life Science for their continuous support.

[1] T. Salerno, P. Donato, G. Frison, L. Zamengo, L. Mondello, *Frontiers in Chemistry*. **2020**, *8*, 624.

Reliability of monodimensional *vs* multidimensional GC-C-IRMS data: a critical evaluation

Danilo Sciarrone[a], Lorenzo Cucinotta[a,b], Gemma de Grazia[a], Luigi Mondello [a,c,d,e]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b] *Department of Food Quality and Nutrition, Research and Innovation Centre, Fondazione Edmund Mach, via Mach 1, San Michele all'Adige, 38010, Italy;*
[c] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, 98168 Messina, Italy*
[d] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, 98168 Messina, Italy*
[e] *Department of Sciences and Technologies for Human and Environment, University Campus Bio-Medico of Rome, Rome, 00128, Italy*

The use of IRMS as a GC detector has a history going back decades, however the critical issue of wrong $\delta^{13}C$ measurements resulting from impure peaks has been often underestimated. To this regard, multidimensional separation techniques are effective tools to improve the consistency of the data, with respect to those obtained after monodimensional analysis.

The present research aims to draw attention to one critical issue, related to the reliability of the $\delta^{13}C$ data obtained by means of monodimensional GC-C-IRMS. Although already known from the literature, such aspect has been often overlooked within the scientific community, as is reflected in the few papers reporting the use of MDGC, among the plethora of published research dealing with GC-IRMS applications.

Hereby, a set of natural samples of complex composition were analysed to investigate the presence of minor or even undetected coelutions, and to which extent this affected isotope ratio determination. If exceeding the monodimensional separation capability, unpredictable co-elutions deriving from exogenous compounds, either resulting from oxidation or intentionally added in fraudulent practices, could also contribute to a shift of the $\delta^{13}C$ data up to 10‰ and higher. Other sources of errors in GC-C-IRMS analysis could be envisaged in natural isotopic abundances, chromatographic effects, and issues related to analytes conversion to CO_2 prior to IRMS measurement.

Based on the results obtained, the implementation of MDGC separation reveals to be mandatory to prevent the aforementioned issues, as illustrated for the selected samples, aiming to guarantee accurate results. Finally, the influence of column bleed is discussed, in that it may affect the determination of the $\delta^{13}C$ data for compounds that are eluted at high temperatures.

Options of 1D GC, flow-modulation signal-enhanced 1D GC and flow-modulation comprehensive 2D GC in a single instrument: a proof-of-concept study

Peter Q. Tranchida [a], Ivan Aloisi [a], Antonio Ferracane [a], Mariosimone Zoccali [b], Luigi Mondello [a,c,d,e]

[a] Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;
[b] Department of Mathematical and Computer Science, Physical Sciences and Earth Sciences, University of Messina, Messina, Italy;
[c] BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;
[d] Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;
[e] Department of Sciences and Technologies for Human and Environment, University Campus Bio-Medico of Rome, Rome, Italy

The present research is focused on the concept of creating three analytical options in a single GC system with two flame ionization detectors (FIDs): 1D GC, flow-modulation (FM) signal-enhanced (SE) 1D GC and FM comprehensive 2D GC (GC×GC). Analyses were performed by using an FM GC×GC instrument (in this case with one FID) equipped with a modulator characterized by seven ports and an external sample loop. Ports 6 and 7 received fractions of first-dimension effluent from the loop, and were connected to a 0.76 m × 0.20 mm ID uncoated column and to a mid-polarity 5 m × 0.32 mm ID × 0.25 µm d_f one. Both columns were characterized by the same pressure drop. When the uncoated column was connected to the FID, then either 1D GC or FM SE GC could be performed. If, on the other hand, the mid-polarity column was linked to the FID, then an FM GC×GC separation was performed. Applications were performed on a bio-fuel and on a mixture of pesticides, with signal-to-noise ratios, limits of quantification and peak widths measured for a variety of analytes under the different analytical circumstances.

Enhanced LC-MS/MS spectra matching through multi-task neural networks and molecular fingerprints

Cecile Valsecchi [a], Giacomo Baccolo [a], Martina Caserta [a], Martina Barbagallo [a], Fabio Gosetti [a], Viviana Consonni [a], Davide Ballabio [a], Roberto Todeschini [a]

[a] Milano Chemometrics and QSAR Research Group, Department of Earth and Environmental Sciences, University of Milano Bicocca, P.za della Scienza 1, Milan, 20126, Italy.

Liquid chromatography tandem mass spectrometry (LC-MS/MS) is routinely used in many clinical applications, including toxicology, drug monitoring, endocrinology, microbiology, and proteomics, thanks to its versatility and effectiveness in the determination of small molecules [1].

The standard approach for analyzing spectral data is the spectral matching that is based on creating a library of annotated spectra against which individual spectrum can be searched for. Building an own spectral library is time-consuming and dependent on the LC-MS/MS instrumentation used, whereas freely available libraries only cover a limited number of molecules [2]. In many cases and especially with newly synthetized substances, the spectrum could not be found in any spectral databases. *In-silico* fingerprints are binary vectors that, through a hashing algorithm, encode features of molecules. Due to their easy computation and instrument-independence, *in-silico* fingerprint databases are bigger and more updated than spectral ones. Prediction of molecular fingerprints starting from the LC-MS/MS spectra would consequently assist the match of any target compound under investigation, which would benefit from the increased dimension of fingerprint databases.

In this study, we developed a multi-task neural network able to predict molecular fingerprints starting from the LC-MS/MS spectra, as depicted in Figure 1. We initially collected and pruned around 70’000 MS spectra from available sources (MassBank of North America [3]). For each compound, fingerprints were calculated (MACCS167 keys [4] and Dragon ECFP of 512 bits) and then multi-task feedforward neural networks were trained to predict the binary bits of molecular fingerprints. Models were validated through specific validation protocols and demonstrated to have suitable performances in terms of predictive accuracy (>85% of bits correctly predicted). Thus, the proposed networks can represent a potential approach for the development of a reliable method to enhance matching of MS spectral data to larger molecular databases. Moreover, with respect to recent studies [5], the proposed model is simple and works with spectra obtained in different experimental conditions.

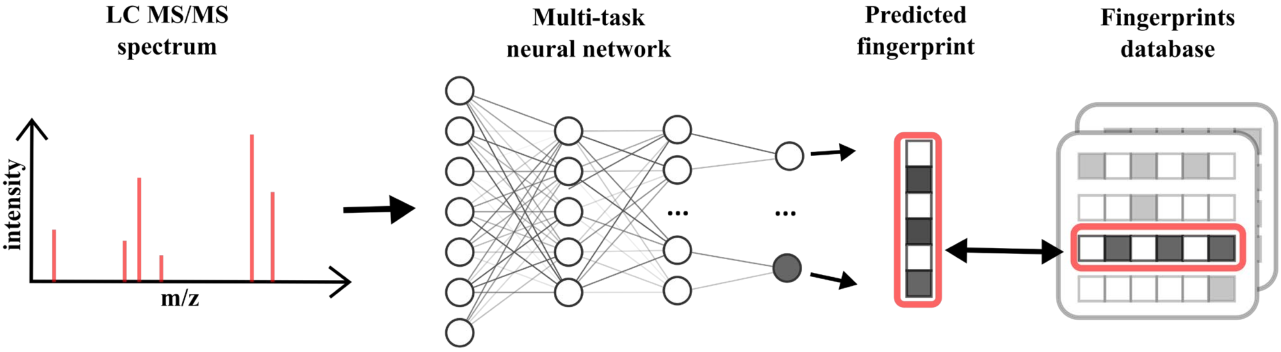


Fig. 1 Workflow for the fingerprint prediction from LC MS/MS through a multi-task neural network and fingerprint matching.

[1] SK. Grebe, RJ. Singh. *Clin Biochem Rev.* **2011**, *32*, 5–31.
[2] H. Lam. *Mol Cell Proteomics.* **2011**, *10*(12), R111.008565.
[3] S. Mehta, https://mona.fiehnlab.ucdavis.edu/
[4] MACCS-II, MDL Information Systems Inc. San Leandro, CA, USA, 1987
[5] H. Ji. *Anal Chem.* **2020**, *92*, 8649-8653.

Evaluation of potential source areas for atmospheric lead reaching Ny-Ålesund (Svalbard) from 2010 to 2019

Francisco Ardini[a], Andrea Bazzano[a], Stefano Bertinetti[a], David Cappelletti[b], Marco Grotti[a]

[a] *Department of Chemistry and Industrial Chemistry, University of Genoa;* [b] *Department of Chemistry, Biology and Biotechnologies, University of Perugia*

Polar regions are the first to be affected by the effects of climatic changes, resulting in fast rises in surface air temperature, reduction of sea ice extent and thickness, warming of the surface waters, and permafrost thawing. Moreover, the Arctic can receive many anthropogenic pollutants via long-range atmospheric transport processes. Hence, a deep comprehension of pollutants' transport mechanisms to the Arctic can provide significant insights into climate change effects, requiring a long-term assessment of their sources, transport pathways and seasonal variations.

Several chemical markers are used to trace the origin of atmospheric aerosol to the Arctic, but lead isotope ratios represent today the most valuable tool for the identification of the source areas of atmospheric particulate matter, having been used in several environmental studies, also in the Arctic. In fact, lead has four stable isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb; the last three are due to the radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively. Consequently, their relative abundance in ores is related to both the abundance of their parent nuclide at the moment of the ore formation, and to the rock's age. Therefore, the study of lead isotopic composition can help to evaluate the different sources of atmospheric particulate matter and, in combination with meteorological data, the movement of air-masses over the mid- and high-latitudes of the Northern Hemisphere.

In the framework of the RIS (Research in Svalbard) projects and the Italian polar research programs, we have carried out a systematic sampling of size-segregated (PM_{10}) atmospheric aerosol at Ny-Ålesund (Svalbard, Norwegian Arctic) in spring and summer seasons from 2010 to 2018. The particulate samples were analyzed for lead content and isotopic composition, evaluating the potential source areas (PSA) through comparison to cluster analysis of back-trajectories. Most of Pb resulted of anthropogenic origin, with an estimated natural contribution from crustal material ranging from 5 to 16%. A strong seasonality was found, with higher concentrations in spring than in summer. In particular, anthropogenic Pb was affected by (i) a Central Asian PSA with Pb isotope signature compatible with ores smelted in the Rudny Altai region, at the Russian and Kazakhstan border, which accounted for 85% of the anthropogenic Pb concentration, and (ii) a weaker North American PSA, contributing for the remaining 15%. During spring 71-86% of samples appeared dominated by the Central Asian PSA without any significant inter-annual variation. On the contrary, 59-87% of summer samples were influenced by the North American PSA, with higher contributions during 2015 and 2018.

Finally, results obtained from the analysis of particulate samples collected in all the seasons of 2019 will be presented, representing the first data of atmospheric lead reaching the area in late autumn and winter.

Strontium isotopic analysis of microsamples by inductively coupled plasma - tandem mass spectrometry

Stefano Bertinetti [a], Eduardo Bolea-Fernandez [b], Frank Vanhaecke [b], Marco Grotti [a]

[a] *Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, 16146, Genoa, Italy;*
[b] *Department of Chemistry, Ghent University, Krijgslaan 281, 9000, Ghent, Belgium.*

In the study of the Southern Hemisphere's atmospheric circulation, the debate about the origins of mineral dust reaching East Antarctica during the Holocene and nowadays is still open [1][2]. In this context, strontium (Sr) isotopic analysis is often used to infer information on the relative importance of the two major sources of dust in the Southern Hemisphere: Australia and Patagonia. Strontium has one radiogenic isotope, ^{87}Sr, deriving from the β^- decay of ^{87}Rb, and the ^{87}Sr/^{86}Sr isotope ratio in a given mineralogical sample depends on the time passed since the formation of the geologic body and its Rb/Sr original composition. Therefore, the ^{87}Sr/^{86}Sr ratio can be used to distinguish crustal dust from different geological contexts.

The precise measurement of the ^{87}Sr/^{86}Sr ratio can be accomplished by inductively coupled plasma-mass spectrometry (ICP-MS). However, the isobaric overlap of ^{87}Rb and ^{87}Sr is a major issue affecting the accuracy of the isotopic analysis, which can be overcome by prior chemical separation of the two elements or by exploiting their different chemical reactivity using ICP-MS instrumentation equipped with collision/reaction cell technology [3]. In addition, when dealing with environmental matrices from Antarctica, the determination of the ^{87}Sr/^{86}Sr isotope ratio brings about additional challenges, such as low analyte concentration and limited sample size, thus requiring minimum sample manipulation and low sample consumption approaches.

In this work, a new method has been developed to realize accurate and precise Sr isotopic analysis of low-volume samples. The ^{87}Sr/^{86}Sr isotope ratios were measured by tandem ICP-MS instrumentation (ICP-MS/MS, Agilent 8800), without prior Sr-Rb separation, and exploiting the selective reaction between Sr and CH_3F/He gas [4]. In order to analyse low-volume samples, the Teledyne-CETAC MVX-7100 µL Workstation has been used. This setup consists of a syringe-driven pump that allows to work at low and stable sample introduction flow rates. The MVX-7100 µL Workstation was combined with a high-efficiency Glass Expansion sample introduction system that was originally designed for the introduction of single cells and other discrete entities into the ICP. Since the effects of the operating parameters on the ICP-MS performance were expected to be inter-related, a multivariate approach was applied to obtain optimum instrument settings [5]. The method thus obtained showed a good reproducibility (RSD = 0.16 ± 0.06 %) and accuracy (relative bias = 0.38 ± 0.85 ‰, with respect to a quality control reference value), consuming only 240 µL of sample with a sample uptake rate of 20 µL/min and a Sr concentration as low as 5.0 µg/L. The applicability of the method was demonstrated by the analysis of digests of soils from Australia and Patagonia, as well as of Antarctic PM_{10} atmospheric dust samples collected in the context of the SIDDARTA project of the Italian Antarctic Research Program (PNRA).

[1] M. Revel-Rolland, P. De Deckker, B. Delmonte, P.P Hesse, J.W. Magee, I. Basile-Doelsch, F. Grousset, D. Bosch, *Earth Planet. Sci. Lett.* **2006**, 249, 1.
[2] P. D. Neff, N. A. N. Bertler, *J. Geophys. Res. Atmos.* **2015**, 120, 9303.
[3] L. J. Moens, F. Vanhaecke, D. R. Bandura, V. I. Baranov, S. D. Tanner, *J. Anal. At. Spectrom.* **2001**, 16, 991.
[4] E. Bolea-Fernandez, L. Balcaen, M. Resano, F. Vanhaecke, *J. Anal. At. Spectrom.* **2016**, 31, 303.
[5] A. Bazzano, M. Grotti, *J. Anal. At. Spectrom.* **2014**, 29, 926.

Photochemistry of furfuryl alcohol in/on snow at -30°C: photoreactivity with singlet oxygen and by direct photolysis.

Luca Carena, Fabrizio Sordello, Claudio Minero*

Department of Chemistry, University of Torino, Via P. Giuria 5, 10125 Torino. (luca.carena@unito.it)

Photochemical reactions can be important transformation pathways for pollutants in the environment. These processes occur naturally in sunlit aquatic systems, such as freshwaters, oceans and in/on snow and ice. In addition to direct photolysis, a photosensitizer able to absorb sunlight, like the chromophoric dissolved organic matter (CDOM), nitrate and nitrite, can produce reactive species (i.e., *Photochemically Produced Reactive Intermediates*, PPRIs), such as hydroxyl radical ($HO^\bullet$), singlet oxygen ($^1O_2$) and CDOM triplet states, that can then react with contaminants, triggering their indirect photodegradation.[1].

Despite occurring at a significantly lower temperature, photoreactions in/on snow and ice have been found to be faster than in liquid water. Such a result has been accounted for by considering that (photoactive) solutes get segregated at grain boundaries of snow/ice during freezing, forming a concentrated, quasi-liquid microenvironment where photochemistry can be very fast [2]. Such a process may affect the environmental fate and quantification of photolabile organic compounds emitted on land and in the oceans, such as pollutants and environmental proxies, eventually deposited on the ice surface in polar regions and alpine glaciers through atmospheric circulation. This makes snow photochemistry worthy of investigation [3] and opens up new frontiers for analytical environmental chemistry.

In this work, the photochemistry of furfuryl alcohol (FFA), a well-known probe compound for $^1O_2$ in liquid solutions [4], was investigated in artificial snow samples at 243 K in the presence of Rose Bengal (RB), here used as photosensitizer for $^1O_2$. FFA photodegradation was assessed through a steady-state irradiation approach, consisting of *(i)* irradiation of properly synthetized snow samples under a visible lamp, *(ii)* collection of snow samples at different irradiation times, *(iii)* sample melting and *(iv)* FFA quantification by means of HPLC-DAD. In the presence of 1 nmol L^{-1} RB, FFA photodegradation followed a pseudo-first order exponential decay at the beginning of the reaction, finally reaching a plateau. We observed a similar kinetic behavior by irradiating FFA samples without RB. These results showed that FFA degradation was a combination of both reactivity with $^1O_2$ and direct photolysis. Moreover, the particular shape of the FFA temporal trends suggested that only a fraction of the compound would be photoactive, while the remaining part, quantified by means of the plateau value, is not. However, the former can be limited by the degradation of the photosensitizer, as assessed through fluorescence measurements. Finally, the dependence of the rate constant of FFA degradation by $^1O_2$ on both FFA and RB concentration allowed the determination of kinetic parameters concerning both the photoproduction and quenching of $^1O_2$, as well as its steady-state concentration in snow.

The comparison among our findings with those reported in the literature showed that FFA photoreactivity with $^1O_2$ would depend on temperature and snow preparation method. Finally, the present results will be at the basis of further investigations on photodegradation of organic compounds, carried out by other PPRIs, such as the excited triplet states of CDOM.

[1] D. Vione, M. Minella, V. Maurino, C. Minero. *Chem. Eur. J.* **2014**, *20*, 10590.
[2] J. P. Bower, C. Anastasio. *Environ. Sci.: Processes Impacts* **2014**, *16*, 748.
[3] A. M. Grannas, A.E. Jones et al. *Atmos. Chem. Phys*. **2007**, *7*, 4329.
[4] F. L. Rosario-Ortiz, S. Canonica. *Environ. Sci. Technol.* **2016**, *50*, 12532.

Year-round records of bulk aerosol composition over the Victoria Land (Antarctica)

Silvia Illuminati[a], *Flavio Vagnoni*[a], *Eleonora Conca*[b], *Anna Annibaldi*[a], *AnnaMaria Falgiani*[a,c], *Federico Girolametti*[a], *Matteo Fanelli*[a], *Giada Giglione*[a], *Davide Vione*[b], *Mery Malandrino*[b] *and Cristina Truzzi*[a]

[a]*Department of Life and Environment Sciences, Università Politecnica delle Marche, Ancona, 60131, Italy*
[b]*Department of Chemistry, University of Turin, Torino, 10125, Italy*
[c]*Regional Agency for Environmental Protection (ARPA), Ascoli Piceno, 63100, Italy*

Atmospheric depositions (dry depositions of particles, wet depositions, and occult depositions by fog and mist) are the most important processes through which atmospheric pollutants are removed and transferred to terrestrial and aquatic ecosystems [1]. The possibility to carry out long-term studies, without or with very limited logistic support, and to identify the sources of pollutants transported at long and short distance makes atmospheric depositions a key role matrix.

The aim of this work was to study the intra- and inter-annual evolution of the atmospheric depositions of different trace elements and major constituents in the Victoria Land region, in order to extend the knowledge on the aerosol chemical composition (until now spatially restricted to very few areas of Antarctica) and to establish potential differences between continental and coastal contributions.

From 2017 to 2020, atmospheric depositions were sampled using bulk collectors (consisting of a polyethylene funnel connected to a bottle of the same material) placed in proximity of ten continental and coastal Antarctic sites corresponding to the automatic weather stations of the Meteo-climatological Observatory of the Italian Antarctic Programme (Fig. 1). The samples were de-freezed and filtrated to separate the soluble and insoluble fractions of the atmospheric particulate. Cellulose mixed ester membrane filters were also weighed to determine the mass concentration of the particulate matter. The soluble and insoluble fractions of major (Na, Ca, K, Mg) minor (Al, Fe, Mn, Zn) and trace elements (As, Cd,Co, Cr, Cu, Hg, Ni, Pb, Se, V) were analyzed by HR-ICP-MS, AAS, and DMA.

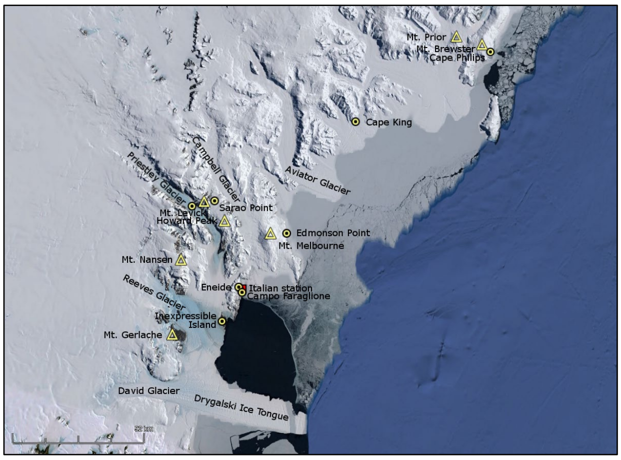


Figure 1. Map of the study area

Enrichment Factors (EFs) and the chemometric treatment of results allowed to assess a main subdivision of the analytes based on primary sources (crustal, marine or anthropogenic source). The main source of atmospheric depositions in the Victoria Land was the sea spray aerosol. A different situation was observed in the proximity of the Italian Antarctic Station "Mario Zucchelli" (MZS) where the chemical composition of atmospheric depositions seemed to be affected by the station activities. Results showed, moreover, the effect of seasonality with depositional fluxes increasing during summer due to (1) pack ice melting with the following release of relevant quantities of sea spray aerosol (and therefore of the typical marine elements, i.e. Na, Ca, K, and Mg) and (2) snowfall from the second half of January.

Excepting for some higher values, depositional fluxes of the studied elements can be considered as natural background values of the atmospheric particulate.

[1] Amodio M., Catino S., Dambruso P. R., de Gennaro G., Di Gilio A., Giungato P., Liola E., Marzocca A., Mazzone A., Sardaro A., Tutino M. (2014) Adv Meteorol, 1.

Identification of aloe and other dyes by means of SERS and HPLC-DAD-MS in the embroidery of a 15th century English folded almanac

Elisa Calà[a], Annalisa Salis[b], Gianluca Damonte[b], Stefania Signorello[c], Elma Brenner[c], Jacqui Carey[d], Maurizio Aceto[a,e]

[a] *Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università degli Studi del Piemonte Orientale, viale Teresa Michel, 11 - 15121 Alessandria, Italy. Email elisa.cala@uniupo.it (E.C.), maurizio.aceto@uniupo.it (M.A.).*

[b] *Center of Excellence for Biomedical Research (CEBR), Università degli Studi di Genova, viale Benedetto XV, 5 - 16132 Genova, Italy. Email annalisa.salis@unige.it (A.S.), gianluca.damonte@unige.it (G.D.).*

[c] *Wellcome Collection, 183 Euston Road, London NW1 2BE, United Kingdom. Email s.signorello@wellcome.org (S.S.), e.brenner@wellcome.org (E.B.).*

[d] *Carey Company, Summercourt Ridgeway, Ottery St. Mary EX11 1DT, United Kingdom. Email jacqui@careycompany.com.*

[e] *Centro Interdisciplinare per lo Studio e la Conservazione dei Beni Culturali (CenISCo), Università degli Studi del Piemonte Orientale, Italy.*

The folded almanac Western MS.8932 (Wellcome Collection, London), produced in England between 1387 and 1405, is a remarkable artefact; it is a calendar with astrological tables and diagrams used by medical practitioners to harness astrological information relating to health. Apart from the great interest for its use in medicine, this object has a unique feature in its exquisite, unique embroidered binding that indicates a prestigious artefact. Considering the scarceness of information on the materials used for its outstanding embroidery, MS.8932 represents an unrivalled opportunity to learn more about production methods relating to embroidery from the medieval period. A diagnostic campaign has been carried out in order to identify the dyes used in the embroidery and evaluate them with reference to their commercial value. Preliminary information on the dyes was yielded by means of UV-visible diffuse reflectance spectrophotometry with fibre optics (FORS) and spectrofluorimetry with fibre optics (FOMF). Then a final identification was achieved by means of micro-invasive techniques such as Surface Enhanced Raman Spectroscopy (SERS) and High Performance Liquid Chromatography-Diode Array Detector-Mass Spectrometry (HPLC-DAD-MS)[1]. Despite the small size of the micro samples (ca. 5 mm of very thin threads), it was possible to identify orchil for pink hues, indigo/madder double dyeing for purple hues, red safflower for salmon pink hues and indigo/weld double dyeing for green hues. Particularly remarkable was the additional identification of aloe in the purple threads, possibly used as mordant and/or as antibacterial agent, which evidence is the first ever recorded in such materials. This information will enable comparisons to be made, helping to situate the artefact and understand its significance.

[1] J.P. Gumbert, Bat Books. A Catalogue of Folded Manuscripts Containing Almanacs or Other Texts, Brepols Publishers, Turnhout, **2016**

Rediscovering the lost color. Advanced vector quantization algorithm and hyperspectral imaging for digital restoration of color films.

Lingxi Liu[a,b], Emilio Catelli[a], Giorgia Sciutto[a], Matija Milanic[c], Silvia Prati[a], Marc Walton[d] and Rocco Mazzeo[a]

[a] *University of Bologna, Department of Chemistry "G. Ciamician", via Guaccimanni, 42 - Ravenna (IT)*
[b] *University of Bologna, Department of Informatics - Science and Engineering, Mura Anteo Zamboni, 7 - Bologna (IT)*
[c] *University of Ljubljana, Faculty of Mathematics and Physics, Jadranska ulica, 19 - Ljubljana (SLO)*
[d] *Northwestern University, Center for Scientific Studies in the Art, 2145 Sheridan Road, Evanston, IL (US)*

Color films were introduced at the beginning of the 20th century with the development of dye-based methods used to give color to moving images. Shortly thereafter, it was found that the dyes used in the coloring procedure were unstable and suffered irreversible processes of color degradation. Nowadays, it is widely acknowledged that the best method to preserve and restore degraded color films uses digital technology. An RGB scanner is usually employed to scan the movies whose color is restored by a dedicated software. This restoration procedure lacks of a systematic approach and often reflects the restorer's personal skill and choice. To overcome these drawbacks, a novel and more automatic digital restoration approach is proposed. Data obtained with a visible hyperspectral imaging (VIS-HSI) are processed using a new vector quantization algorithm, similar to k-means clustering, which allows for the reconstruction of the original color (or the closest to the original) in degraded areas of the frames.
The instrument used to scan the films is a custom-made hyperspectral camera (380 – 780 nm), specifically built to have high spatial and spectral resolution performances. The advantage of combining HSI and the vector quantization algorithm is represented by the possibility of describing the degradation patterns through a set of representative spectra, taking into account the chemical-related information of the differentially degraded color areas on historical film samples. The proposed algorithm uses one reference image representing the best preserved of each scene and a collection of degraded images from the same scene. The reference image is used as a source of "good" spectra. A pixel-to-pixel correspondence between the reference and degraded images allows to replace the spectra in a damaged image and obtain the restored one. Four degraded positive frames, showing evident degradation and fading effects, were successfully restored with the proposed method. Results demonstrate that hyperspectral imaging combined with an *ad hoc* vector quantization algorithm may be successful in the restoration of damaged motion pictures with an objective color reconstruction.

Acknowledgments:
We thank *L'immagine Ritrovata* – film restoration and conservation - for providing the samples used in the research. We acknowledge the financial support from the Italy-Slovenia bilateral cooperation program in science and technology.

The Third-Century monetary crisis: chemical analysis of Denarii and Antoniniani

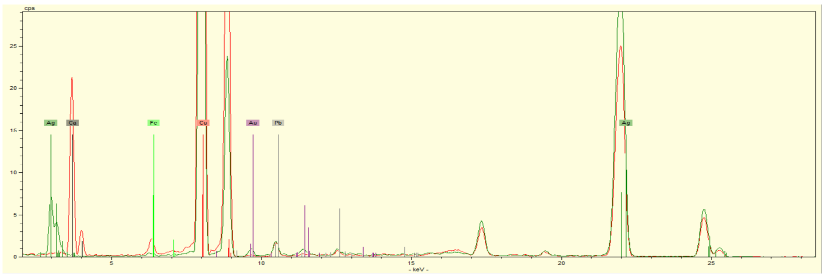
G. Marussi[a], M. Crosera[a], E. Prenesti[b], B. Callegher[c], G. Adami[a]

[a] Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via L. Giorgeri, Trieste, Italy; [b] Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria, 5, Torino, Italy; [c] Dipartimento di Studi Umanistici, Università di Trieste, Via del Lazzaretto Vecchio 8, Trieste, Italy

Analytical chemistry plays a crucial role in the characterisation of cultural heritage and in supporting archaeometric studies. The combination of non-destructive techniques with micro-destructive techniques, which are more informative, is essential to gain more information about the composition of the "bulk" (the innermost part) of the objects and not only regarding the surface [1], [2].
In this work, we adopted an optimised method from the University of Trieste suitable for destructive and non-destructive chemical analysis of ancient coins. It has been used for the study of folles (copper coins of the 10th century) [3] and late antique gold solids (Gratian-Justin I, 4th-6th centuries) [4].

A set of 160 Denarii and Antoniniani (silver or silver alloy coins of the 3rd century) from a hoard found in the Balkan area, now kept in the Numismatics Laboratory of DiSU (University of Trieste) was analysed [5]. Initially, a non-destructive elemental analysis was performed by an ARTAX 200 micro-XRF spectrometer (supplied by Bruker Nano GmbH), followed by a micro-destructive ICP-MS analysis with a NexION 350x Spectrometer (PerkinElmer, USA) equipped with an ESI SC Autosampler. Thus, information related on the surface and mass composition of the samples was obtained and these results may be correlated with the socio-economic situation of the historical period.

The processing of the μ-XRF spectra collected for each coin revealed the presence of elements such as Ag, Cu, Au, Pb, Zn, Fe and Ca (the latter being present in the concretions, suggesting the deposition of $CaCO_3$). The subsequent destructive ICP-MS analysis will be focused on these specific elements, in order to determine their concentration in the coin specimens.



[1] R. Mazzeo, A. Roda, e S. Prati, *Anal. Bioanal. Chem.*, **2011**, 399, 9, 2885.
[2] A. Adriaens, *TrAC Trends Anal. Chem.*, **2004**, 23, 8, 583.
[3] M. Crosera, E. Baracchini, E. Prenesti, A. Giacomello, B. Callegher, P. Oliveri, G. Adami, *Microchem. J.*, **2019**, 147, 422.
[4] G. Marussi, I. Carlomagno, G. Aquilanti, M. Amati, P. Zeller, M. Crosera, E. Prenesti, B.Callegher, G. Adami, *SPIE Optical Metrology*, **2021**.
[5] For the provenance: B. Callegher, *Department of Humanities. University of Trieste*, "International Numismatic News", **2014**, 17, 5-7.

Synthesis and spectroscopic characterization of synergistic nanomaterials for stone artwork protection

R.A. Picca, M. Izzi, M.C. Sportelli, L. Sabbatini, N. Cioffi

Chemistry Department, University of Bari Aldo Moro, via E. Orabona 4, 70126 Bari, Italy

Deterioration of buildings and heritage monuments represents a global concern which has been addressed in the last decades by exploring novel strategies involving smart nanomaterials. In particular, biodeterioration and consolidation of stone artworks can be tackled by developing and applying suitable nanostructured materials. In this sense, antimicrobial and consolidating properties of some inorganic oxides (e.g. ZnO) [1] and hydroxides (e.g. $Ca(OH)_2$) [2] nanostructures are interesting alternatives to other conventional approaches applied in this field. Moreover, the combination of different properties in a single multifunctional stone treatment could improve significantly the protective action. For example, a synergistic treatment combining silver and silica nanoparticles as well as a coating implementing $Ca(OH)_2$ and ZnO/TiO_2 have been proposed recently [3,4]. On the other hand, it is also desirable to prepare new nanostructures following eco-compatible synthetic routes reducing the impact of toxic species [5].

In this communication, a one-step synthesis of hybrid ZnO-$Ca(OH)_2$ nanostructures is reported. For the first time, the sacrificial anode electrolysis method for the synthesis of ZnO nanoparticles (NPs) [5] is combined with a conventional approach for the synthesis of colloidal $Ca(OH)_2$ NPs [6]. In this way, $Ca(OH)_2$ and ZnO NPs grow simultaneously in the same medium. In fact, a NaOH solution acts as both electrolytic medium and source of hydroxyl ions. Hence, the zinc electrode is immersed in the alkaline solution and $CaCl_2$ is added at a controlled rate during the electrosynthesis. The process is performed under continuous stirring at a controlled temperature in deaerated conditions. A whitish precipitate is obtained, dried overnight at 120°C. A detailed morphological (TEM) and spectroscopic (FTIR, XPS) characterization of the as-prepared powders provides useful information about the physico-chemical properties of the nanomaterials. It has been observed that a proper tuning of sodium hydroxide concentration influences not only the yield of the process, but also the morphology and composition of the resulting nanostructures. The hybrid nanomaterials have been brushed on sanded glasses and stone samples, in order to investigate the features of the innovative coatings in terms of contact angle and carbonatation process as starting point for their perspective application for carbonatic stone preservation.

[1] Ditaranto, N., I. D. van der Werf, R. A. Picca, M. C. Sportelli, L. C. Giannossa, E. Bonerba, G. Tantillo, and L. Sabbatini. 2015. *New Journal of Chemistry* 39 (9): 6836–43.

[2] Baglioni, Piero, David Chelazzi, Rodorico Giorgi, and Giovanna Poggi. 2013. *Langmuir* 29 (17): 5110–22.

[3] R. Zarzuela, M. Carbú, M.L.A. Gil, J.M. Cantoral, M.J Mosquera, Nanotechnology 30 (2019) 345701.

[4] Gómez-Ortíz, N., S. De la Rosa-García, W. González-Gómez, M. Soria-Castro, P. Quintana, G. Oskam, and B. Ortega-Morales. 2013. *ACS Applied Materials & Interfaces* 5 (5): 1556–65.

[5] Sportelli, M. C., R. A. Picca, M. Izzi, G. Palazzo, R. Gristina, M. Innocenti, L. Torsi, and N. Cioffi. 2020. *Nanomaterials* 10 (3): 473.

[6] Ambrosi, M., L. Dei, Rodorico Giorgi, Chiara Neto, and Piero Baglioni. 2001. *Langmuir* 17 (14): 4251–55.

Printing Biology: engineering analytical platforms by molecular inks

Giuseppe Arrabito,[a] Bruno Pignataro[a]**

*[a]Department of Physics and Chemistry – Emilio Segrè, University of Palermo, viale delle Scienze, bdg. 17, Palermo 90128, Italy. * emails: giuseppedomenico.arrabito@unipa.it; bruno.pignataro@unipa.it.*

The assembly of life-like artificial biosystems allows understanding the molecular origins of life, whilst guiding the nature-inspired development of analytical platforms suitable for many applications, as for instance in molecular sensing, lab-on-chip, point-of-care diagnostics [1]. These systems mimic and even improve the functional features of biological systems, reproducing their collective behaviors, fine organization, and adaptivity to environmental stimuli [2]. This work shows the possibility to readily produce these systems by an integrative approach we herein define as *Printing Biology* [3], a new research field which stems from the emerging world of additive manufacturing and the bottom up Synthetic Biology fabrication. *Printing Biology* allows the fabrication of artificial biosystems at different scales (from nanometers up to millimeters) and variable chemical composition (DNA, proteins, phospholipids), showing functionalities allowing the determination of molecular interactions and features in conditions mimicking living systems. This work shows analytical platforms realized by inkjet printing (IJP) and microcantilever spotting (μCS). The molecular inks are dispensed in the form of aqueous or non-aqueous compartments, whose volume typically spans from femtoliter (10^{-15} L) up to picoliter (10^{-12} L) scales. The coefficient of variation of the dispensed droplets is typically below the 3%, allowing for excellent reproducibility in the deposition process. The dispensed droplet spacing can be tuned in order to obtain a final sessile droplet with a volume at higher scales (up to nanoliter or event microliter scale). The formulation of molecular inks will be in particular analyzed, taking into consideration all the most relevant parameters (e.g. viscosity, ionic force, surface tension, solute-solvent interactions) which guide the deposition process and the activity retaining of the dispensed biomolecules [4]. The analytical determination of the dispensed molecules will be carried out by employing optical detection, in particular fluorescence intensity and fluorescence lifetime. Three different ink printable formulations will be employed, including DNA, proteins and phospholipids. The dispensed systems will be determined by analyzing their molecular content (down to few zeptomoles) and molecular conformation within the dispensed droplet. Three representative examples will be shown. The first is the formulation of DNA oligonucleotides fL-scale ink imbibition by μCS into nylon to realize a flexible sensor for DNA detection [5]. The second is the realization of stable pL- or fL-scale aqueous compartments stabilized in mineral oil to study molecular interactions in restricted volumes, permitting to highlight the effect of molecular crowding in compartments mimicking sub-cellular scale systems [6]. Finally, the fabrication of phospholipids by μCS onto glass surfaces is reported, allowing for membrane-protein interaction studies at solid-liquid interfaces.

[1] H. Jia, P. Schwille, *Curr. Opin. Biotechnol.* **2019,** *60*, 179.
[2] B.C. Buddingh', J.C.M. van Hest, *Acc. Chem. Res.* **2017**, *50*, 769.
[3] G. Arrabito, B. Pignataro, *Small*, **2020**, *16*, 1907691.
[4] G. Arrabito, B. Pignataro, *Anal. Chem.* **2013,** *84*, 5450.
[5] G. Arrabito, V. Ferrara, A. Ottaviani, F. Cavaleri, S. Cubisino, P. Cancemi, Y.P. Ho, B.R. Knudsen, M.S. Hede, C. Pellerito, A. Desideri. S. Feo, B. Pignataro, *Langmuir*, **2019,** *35*, 17156.
[6] G. Arrabito, F. Cavaleri, A. Porchetta, F. Ricci, V. Vetri, M. Leone, B. Pignataro, *Adv. Biosys.*, **2019,** *3*, 1970074.

Design of dual-functional polymer on plasmonic biosensor for detection of circulating tumor DNA point mutations

Noemi Bellassai[a], Roberta D'Agata[a,b], Almudena Marti[c], Andrea Rozzi[d], Stefano Volpi[d], Matteo Allegretti[e], Roberto Corradini[b,d], Patrizio Giacomini[e], Jurriaan Huskens[c], Giuseppe Spoto[a,b]

[a] *Department of Chemical Sciences, University of Catania, Viale Andrea Doria 6, 95122, Catania, Italy.*
[b] *INBB, Istituto Nazionale di Biostrutture e Biosistemi, Viale delle Medaglie d'Oro, 305, 00136 Roma, Italy.*
[c] *Department of Molecules & Materials, MESA+ Institute for Nanotechnology, Faculty of Science & Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.*
[d] *Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parco Area Delle Scienze, 17/A, 43124, Parma, Italy.*
[e] *Oncogenomics and Epigenetics, IRCSS Regina Elena National Cancer Institute, Via Elio Chianesi, 53, 00144 Rome, Italy.*

Circulating tumor DNA (ctDNA) represents an emerging blood-based biomarker in liquid biopsy for early cancer diagnosis, monitoring, and determining prognosis [1]. Nowadays, standard protocols for ctDNA analysis include complex sample handling and time-consuming pre-analytical procedures (e.g. sequence isolation and amplification), risks for sample contamination, and assay costs which represent critical issues in pre-analytical steps [2]. Lately, a nanoparticle-enhanced surface plasmon resonance imaging-based assay to simplify the direct detection of tumor DNA in the patient's plasma has been developed [3]. To further streamline the workflow analysis, we herein propose a new dual-functional low-fouling poly-L-lysine (PLL)-based polymer with nanoparticle-enhanced surface plasmon resonance biosensing for the detection of circulating tumor DNA point mutations related to colorectal cancer in human plasma [4]. The PLL-based polymer contains densely immobilized anionic oligopeptide side-chains to create a charge-balanced system repelling the non-specific adsorption of undesired biomolecules onto the sensor surface. The layer also includes sparsely attached peptide nucleic acid probes, complementary to DNA target sequences, capturing the analyte directly in human plasma. First, we thoroughly explored the role of each component of the dual-functional polymer to the antifouling capability. Then, the low-fouling activity of the new surface layer assured us to detect KRAS p.G12D mutated DNA in human plasma at the attomolar level (~ 2.5 aM), and KRAS p.G13D mutated DNA in a liquid biopsy from a colorectal cancer patient. The work here described offers a rapid, simple, and label-free ultrasensitive detection of tumor-derivated materials circulating in biological fluids with minimal pre-analytical sample treatments and without blocking additives after the plasma adsorption, making a significant improvement for early clinical diagnosis and personalized medicine in liquid biopsy.

[1] D.W. Cescon, S. Bratman, S.M. Chan, L. L. Siu, *Nat. Cancer.* **2020**, *1*, 276–290.
[2] T. Gerber, S. Taschner-Mandl, L. Saloberger-Sindhöringer N. Popitsch, E. Heitzer, V. Witt, R. Geyeregger, C. Hutter, R. Schwentner, I. M. Ambros, P. F. Ambros, *J. Mol. Diagn.* **2020**, *22*, 8, 1070–1086.
[3] R. D'Agata, N. Bellassai, M. Allegretti, A. Rozzi, S. Korom, A. Manicardi, E. Melucci, E. Pescarmona, R. Corradini, P. Giacomini, G. Spoto, *Biosens. Bioelectron.* **2020**, *170*, 112648.
[4] N. Bellassai, R. D'Agata, A. Marti, A. Rozzi, S. Volpi, M. Allegretti, R. Corradini, P. Giacomini, J. Huskens, G. Spoto, *ACS Sens.* **2021**, in press.

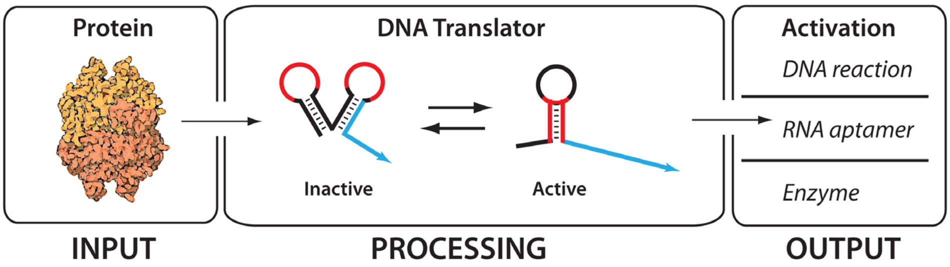
Artificial Biomolecular Communication Regulated by Synthetic DNA Translators

Alessandro Bertucci, [ab] *Alessandro Porchetta,* [b] *Erica Del Grosso,* [b] *Francesco Ricci* [b]

[a] *Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy;* [b]*Department of Chemical Sciences, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, Italy.*

Interfacing DNA-based computation with complementary biomolecular systems, such as proteins, enzymes or RNA, will provide us with enhanced ability to process molecular information and to generate custom function. We have engineered synthetic DNA translators that, through a programmable conformational change, are able to convert specific protein-binding events into inputs for triggering DNA-based dynamic molecular operation.[1] This allowed us to establish artificial communication between diverse biomolecular species and create bio-synthetic functional networks. Specifically, we have constructed synthetic DNA-based systems responsive to two different DNA-binding proteins: TATA-binding protein and Myc-Max transcription factor complex. A specific DNA translator recognized by its target protein is designed to switch from an inactive to an active conformation upon protein binding and to actuate DNA-based molecular operations. We have optimized the thermodynamic and kinetic properties of the system and demonstrated that a DNA strand displacement reaction can be remotely controlled by using a specific DNA-binding protein as an upstream input. We have then extended our strategy to the control of multi-input orthogonal strand displacement reaction networks. Eventually, we established new forms of artificial DNA-based biomolecular communication and introduced protein-controlled activation of a fluorescent synthetic RNA structure and regulation of the proteolytic activity of an enzyme non-naturally related to the input DNA-binding protein. Our study provides new biomolecular design strategies that will allow many other DNA-binding proteins to be utilized as molecular inputs for guiding DNA-based computation and creating new functional pathways in synthetic biology. As further complex molecular operations aimed at controlling 3D self-assembly, performing advanced protein sensing and processing biomolecular information through higher-order circuits may be envisioned, our system may enable a wide range of new applications in synthetic biology, DNA nanotechnology, bioanalytical chemistry and life sciences in general.

[1] A. Bertucci, A. Porchetta, E. Del Grosso, T. Patiño, A. Idili, F. Ricci, *Angew. Chem. Int. Ed.* **2020**, *59*, 20577.



Soft molecularly imprinted nanoparticles for protein recognition in sensing and assays

Alessandra Maria Bossi[a]

[a] *Università di Verona, Dipartimento di Biotecnologie, Strada Le Grazie 15, Verona*

Molecularly imprinted polymers (MIPs) are biomimetics prepared by a template assisted synthesis [1]. MIPs possess exquisite selectivity, robustness, cost-effective synthesis, integrability to electronics and can be stimuli-responsive. When synthesized in nanometric format, MIP nanoparticles (MIP NPs) are colloquially referred to as "plastic antibodies" [2].

Over the last years, MIP NPs suitable to target protein biomarkers have been raising considerable interest. For the success of protein-addressed MIP NPs, which strategy to use when stamping macromolecular binding sites represents the crucial choice [3]. The imprinting of epitopes, i.e. a small portion of the protein template, for preparing successful protein-recognition MIP NPs seems to provide a general route [3].

The so prepared protein-selective MIP NPs find application in optical sensing [4,5], in electrochemical sensing and in assays [6,7].

[1] G. Wulff and A. Sarhan, *Angew. Chem. Int. Ed.* **1972**, *11*, 341; R. Arshady and K. Mosbach, *Die Makromoleculare Chemie* **1981**, *182*, 687.
[2] K. Haupt, *Nat Mater.* **2010**, *9*, 612.
[3] L. Pasquardini, A.M. Bossi, *Anal. Bioanal. Chem.* **2021**, https://doi.org/10.1007/s00216-021-03409-1.
[4] A. Chiappini, L. Pasquardini, A.M. Bossi, *Sensors* **2020**, *20*, 5069.
[5] N. Cennamo, D. Maniglio, R. Tatti, L. Zeni, A.M. Bossi, *Biosensors & Bioelectronics* **2020**, *156*, 112126.
[6] L. Cenci, C. Piotto, P. Bettotti, A.M. Bossi, *Talanta* **2018**, *178*, 772.
[7] M. You, S. Yang, W. Tang, F. Zhang, P.-G. He, *ACS Appl. Mater. Interfaces* **2017**, *9*, 13855.

A microfluidic paper-based chip patterned with Prussian Blue to determine sweat urea

Stefano Salatiello [a], Chiara Cassiano [a], Stefano Cinti[a,b,]*

[a] Department of Pharmacy, University of Naples "Federico II", Via D. Montesano 49, 80131 Naples, Italy; [b]BAT Center - Interuniversity Center for Studies on Bioinspired Agro-Environmental Technology, University of Napoli Federico II, 80055 Naples, Italy. e-mail: stefano.cinti@unina.it;

The search for analytical strategies to ensuring clinical monitoring, without recurring the use of laboratory and skilled personnel, is highly required. However, the development of brand-new Point-of-Care devices cannot overlook the successful combination among manufacture methodologies, functional (smart)materials, and transduction mechanisms. In particular, the era of sustainability we belong in, strictly requires user-friendly and low-cost approaches, adaptable in low-resource contexts, i.e. developing world.

Recently, wearable devices have attracted extensive attention in the fields of healthcare, owing to their conformal contact with soft skins or organs and continuous monitoring of physiological state

As the case of study, the detection of urea in sweat samples has been considered. Moreover, urea is an important nitrogen metabolite in body fluids (e.g., serum, urine, and sweat) and also one of the markers of renal function and heart metabolic disorders clinically, and people with hepatic or renal failure, or uremia have significantly higher levels of the toxic ingredient urea in their sweat than the normal.

Despite all the optical and electrochemical approaches reported to date, we decided to exploit chromatographic papers in order to realize a novel miniaturized analytical tool. The porous structure of paper allowed both to be patterned with Prussian Blue Nanoparticle and to load the enzyme urease necessary to evaluate the presence of urea (enzymatic substrate). The use of wax printing allowed fabricating a paper-based microfluidic platform for multi-measure purposes. Briefly, when urea is present in the sample, urease converts the substrate into carbon dioxide and ammonia. Ammonia makes the pH increases and the final effect is the removal of iron ions from Prussian Blue structure, forming $Fe(OH)_2$, with the result of production of a colorless solution. The observed fading is proportional to the presence of urea, and thus to the enzymatic activity.

However, the structure of paper reveals its importance in loading reagents, preconcentrating and filtering complex matrices, going beyond some issues associated with colorimetric methods. Herein, the experimental procedure for Prussian Blue use has been finely optimized with a chemometrics-based DoE (paper type, geometry, precursor concentration, sampling volume, enzyme amount) and the detection of urea has been carried out linearly in the mM range, that is the physiological range for urea in sweat samples. Recovery tests have been performed by spiking sweat with different levels of urea, obtaining percentage recoveries between 95-105%. The accuracy of the portable Prussian Blue-based platform was evaluated in sweat samples collected from volunteer. In addition, a satisfactory correlation has been obtained in comparison with mass spectrometry analyses.

Transient control of DNA-based systems

E. Del Grosso [a,b]*, L. J. Prins* [c] *, F. Ricci* [a]*.*

[a] *Department of Chemistry, University of Rome, Tor Vergata, Rome, Italy;* [b]*Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California;* [c]*Department of Chemical Sciences, University of Padua, Padua, Italy.*

A strong current interest in the field of supramolecular chemistry is the development of molecular devices with features characteristic of living organisms. The possibility to create synthetic materials or devices with transient properties can lead to adaptable systems with unprecedented properties. Has been recently demonstrated that synthetic DNA, thanks to the high programmability and predictability of nucleic acids, is particularly suited for designing out-of-equilibrium systems.

Recently we provide several examples of kinetically controlled DNA-based systems. Some of them rely, like naturally occurring examples, in the use of enzymes as fuel consuming units to return the system to the initial condition. Although highly efficient, enzymes pose limits in terms of long term stability and inhibition of enzyme activity by waste products. Motivated by the above arguments, we also demonstrate the possibility to kinetically control DNA-based systems through a non-enzymatic chemical reaction. More specifically, inspired by the redox signalling employed by cells to control cellular processes, we employ redox cycles of disulfide-bond formation/breakage to kinetically control the assembly and disassembly of DNA-based tubular nanostructures in a highly controllable and reversible fashion.

The exploitation of redox chemistry as a new control mechanism will facilitate the implementation of fuelled-DNA self-assembly processes in a synthetic context.

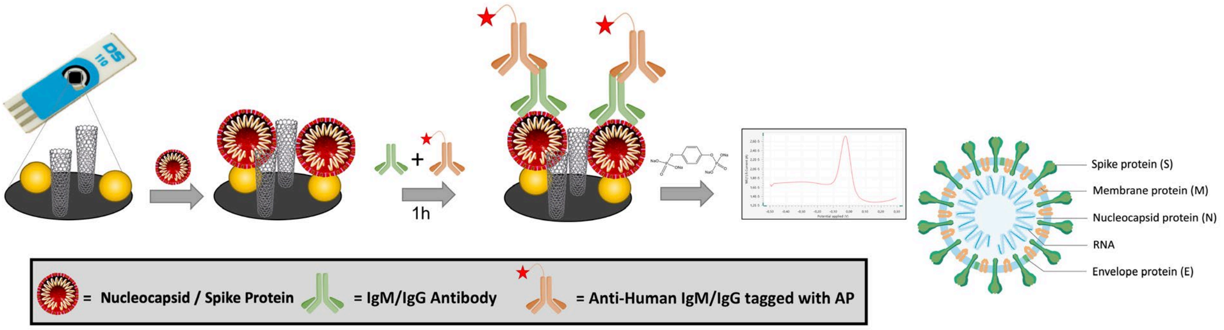
[1] E. Del Grosso,, L. J. Prins, F. Ricci. *Angew. Chem. Int. Ed***. 2020**, *59*, 13238.

Smart immunosensors for point-of-care serologic test to determine the level of immunity by Covid-19 infection or by SARS-CoV-2 vaccination

Marco Giannetto[a] *Simone Fortunati*[a], *Chiara Giliberti*[a], *Davide Ferrari*[a], *Massimo Locatelli*[b], *Angelo Bolchi*[a], *Valentina Bianchi*[c], *Andrea Boni*[c], *Ilaria De Munari*[c], *Maria Careri*[a]

[a]*Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17/A, Parma, Italy;* [b]IRCCS *San Raffaele Hospital, Via Olgettina 60, Milan, Italy;* [c]*Department of Engineering and Architecture, University of Parma, Parco Area delle Scienze 181/A, Parma, Italy.*

Smart portable devices suitable for non-hospital environments can be an efficient solution for rapid screening of the immunization status of the population, especially in emergency situations such as the SARS-CoV-2 pandemic. In this context, we developed innovative electrochemical immunosensors based on disposable screen-printed electrodes functionalized with nucleocapsid (N) or spike (S1) viral proteins for the determination of the respective IgG and IgM antibodies. These functional neutralising specific antibodies, produced following infection, vaccination, or both represent possible biomarkers for evaluating natural immunity (anti-N and anti-S1) and vaccine-acquired immunity (anti-S1) to COVID-19. In the case of sensors developed for detection of anti-N antibodies, gold nanoparticle assembly on carbon nanotubes allowed us to effectively immobilize the N-protein and amplify the response. Immunoabsorbed antibodies were detected by alkaline phosphatase-tagged anti-human IgG and IgM [1]. These immunosensors were successfully validated in human serum according to guidelines for epidemiological studies [2], showing excellent performance in terms of accuracy (90%), precision (100%), specificity (100%) and sensitivity (80%), as attested by comparison with chemiluminescence assay results from DiaSorin (LIAISON SARS-CoV-2 S1/S2) and Roche (Elecsys Anti-SARS-CoV-2 and Elecsys Anti-SARS-CoV-2-S), making the current strategy promising for point-of-care testing (POCT). The biosensor for anti-S1 determination gave promising results suitable for assessment of immunization in vaccinated subjects.



Concerning the signal readout, an electrochemical portable and battery-operated IoT device equipped with a WiFi module and developed to maximize the resolution was specifically designed for autonomous calibration and onboard data processing [3]. Operations in different fields of application are possible through a web-based set-up of electrical parameters, exploiting cloud services for data storage and processing. Although still experimental, the characteristics of this approach make it a promising candidate for a future rapid POCT.

[1] M. Giannetto, V. Bianchi, S. Gentili, S. Fortunati, I. De Munari, M. Careri, *Sens Actuators B Chem*. **2018**, *273*, 1395.
[2] Z. Wen, N. Zeng, N.Wang, *NESUG proceedings: health care and life sciences, Baltimore, Maryland 19 (2010): 67.*
[3] V. Bianchi, M. Mattarozzi, M. Giannetto, A. Boni, I. De Munari, M. Careri, *Sensors*. **2020**, *20*, 2016.

Reagent-free paper biosensor based on genetically modified bioluminescent protein for cancer biomarker detection

Antonia Lopreside [a,b], Laura Montali [a,b], Maria Maddalena Calabretta [a,b], Elisa Michelini [a,b,c]

[a] *Department of Chemistry "G. Ciamician", University of Bologna Via Selmi, 2, Bologna, Italy*
[b] *Centro di Ricerca Biomedica Applicata (CRBA), Azienda Ospedaliero-Universitaria Policlinico S. Orsola-Malpighi, Bologna, Italy*
[c] *INBB, Istituto Nazionale di Biostrutture e Biosistemi, Viale Medaglie d'Oro 305, Roma, Italy*

User-friendly and low-cost biosensors offer unique tools for self-diagnoses and telemedicine. In the recent years, several efforts have been made to develop easy-to-use analytical devices that do not require expensive equipment or skilled personnel. To this end, biosensors based on bioluminescent proteins offer unique tools thanks to their easy handling, high signal, and long-term stability.

Here, we present a bioluminescent biosensor based on Nanoluc Binary Technology (NanoBiT), for cancer screening and monitoring via protease activity detection. High level of metalloproteases has been proven to be involved in tumor progression, metastasis formation and increased drug resistance combined with less chance for patient survival. Real-time monitoring of protein production can also offer a tool for drug response and tumor progression.

The two subunits of Nanoluc luciferase, LgBiT and SmBiT, have been genetically fused with the target sequence recognized by Matrix Metalloproteinase-2 (MMP2) to create a fast and sensitive biosensor based on protein complementation technique. A 6-His tag has been also introduced at protein C'-terminal for cheap protein expression and purification in *E. coli*.

In absence of metalloprotease activity, the sensor structure remains functional, and it produces a bioluminescent signal. Conversely, in the presence of MMP2 protease activity, the BL signals decreases in a quantitative way.

A ready-to-use reagent-free disposable cartridge has been developed lyophilizing both the bioluminescent nanosensor and the substrate into a cheap and eco-friendly paper-based device. On-paper lyophilization offers long-term stability under different storage temperature condition -20°C, +4°C and room temperature.

3D printing technology has been used to design a tunable and reusable device for smartphone interfacing and signal acquisition. Smartphone camera has been implemented as detector for easy signal acquisition to reduce equipment cost and allow easy data storage and labelling.

In optimized conditions we were able to obtain as limit of detection for MMP2 in the nM range with only 30 minutes of incubation with a few µl of sample.

Tipologia: presentazione orale

Selective detection of *Xylella fastidiosa* with a Surface Plasmon Resonance based immunoassay

Lucia Sarcina,[a] *Eleonora Macchia,*[b] *Giuliana Loconsole,*[c] *Giusy D'Attoma,*[c] *Pasquale Saldarelli,*[c]
Vito Elicio [d] *and Luisa Torsi* [a,b,e]

[a] *Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, 70125 Bari, Italy;* [b] *The Faculty of Science and Engineering, Åbo Akademi University, FI-20500 Turku, Finland;* [c] *Institute for Sustainable Plant Protection CNR, Bari, Italy;* [d] *Agritest Srl, Tecnopolis Casamassima, Bari Italy;*
[e] *CSGI (Centre for Colloid and Surface Science), 70125 Bari, Italy*

In the last decade, the *Xylella fastidiosa* bacterium has spread worldwide causing multiple plant diseases, with huge economic impact on agriculture and environment. [1,2] By revealing the presence of the bacterium before symptom arrival, preventive action plans could be applied to confine the contagion. To this aim, the development of a surveillance device, conveying high sensitivity along with early detection of *X. fastidiosa* outbreaks, would be of paramount importance. Fundamental to the development of such a detection system is the availability of high binding affinity antibodies for *X. fastidiosa* (*anti-XF*), which could be integrated in the sensor transducers. Among other bio-sensing techniques, Surface Plasmon Resonance (SPR) holds the advantage of being a label-free detection system, providing real-time monitoring of bio-affinity reactions.[4] So far, a variety of plant pathogen biomarkers were studied by means of SPR, but none of them involves *X. fastidiosa*.[3] In this study SPR has been used to assess an optimized biofunctionalization protocol of gold surfaces with *anti-XF*, validating their capturing efficacy against *X. fastidiosa*. The assay selectivity is guaranteed by the bio-functionalization of gold transducing interfaces with the polyclonal antibodies for *X. fastidiosa,* covalently bounded to a self-assembled monolayer of alkylthiols. Thus, the selectivity was assessed by means of a control experiment with the non-binding *Burkholderia phytofirmans* bacterium. Remarkably, a limit of detection as low as 10^5 CFU/mL was achieved by transducing the direct interaction between the X. fastidiosa bacterium and its affinity antibody, which is comparable to the label-needing ELISA gold standard. Moreover, the binding-affinity between polyclonal antibodies and the *X. fastidiosa* bacteria has been also evaluated, obtaining an equilibrium affinity constant of $3.5 \cdot 10^7$ M^{-1}, comparable with those given in the literature for bacteria detection against affinity antibodies. The study is therefore a preliminary development of a reliable cost-effective process to successfully bio-functionalize a gold surface, eventually suitable as gate electrode in wide-field bioelectronic sensors, for ultra-sensitive detection of *X. fastidiosa*.[5]

[1] C. Cariddi, M. Saponari, D. Boscia, A. De Stradis, G. Loconsole, F. Nigro, F. Porcelli, O. Potere, G. P. Martelli, *J. Plant Pathol.* **2014**, *96*, 425.
[2] P. Baldi, N. La Porta, *Front. Plant Sci.* **2017**, *8, 944.*
[3] A. D. Taylor, J. Ladd, Q. Yu, S. Chen, J. Homola, S. Jiang, *Biosens. Bioelectron.* **2006**, *22*, 752.
[4] V. Nanduri, A. K. Bhunia, S. I. Tu, G. C. Paoli, J. D. Brewster, *Biosens. Bioelectron.* **2007**, *23*, 248.
[5] E. Macchia, K. Manoli, B. Holzer, C. Di Franco, M. Ghittorelli, F. Torricelli, D. Alberga, G. F. Mangiatordi, G. Palazzo, G. Scamarcio, L. Torsi, *Nat. Commun.* **2018**, *9*, 3223.

Nanomaterials for improved sensitivity in sample treatment

Federica Bianchi [a,b], *Nicolò Riboni* [a], *Angela Arcoleo* [a], *Fabio Fornari* [a], *Franco Bisceglie* [a], *Paolo Pelagatti* [a], *Maria Careri* [a,b]

[a] *Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17/A, Parma, Italy;* [b] *University of Parma, Interdepartmental Center for Energy and Environment (CIDEA), Parco Area delle Scienze 42, Parma, Italy*

Environmental pollution is one of the major threats of modern society. The increasing number of anthropic, industrial, and agricultural activities causes the release into the environment of persistent organic pollutants and a variety of newly identified substances known as emerging contaminants (ECs). Although the majority of ECs are not included in routine European monitoring programs, these substances require attention due to their high frequency of occurrence, the suspected health effects and ecotoxicity and the lack of sensitive analytical and sampling techniques. Due to the very low concentration levels in real samples, sample pretreatment is required to achieve analyte enrichment. In addition, the conditions used during the sample preparation process should be carefully optimized to obtain an effective cleanup without analyte losses. In this context, nanomaterials including metal-organic frameworks, supramolecular receptors, polymer-based nanocomposites, and carbon-based structures can be a valuable tool to improve method selectivity and sensitivity.

In the frame of a research activity dealing with the development of novel materials for sample treatment [1,2], the potential of both properly functionalized carbon nanotubes (CNTs) and metal-organic frameworks (MOFs) [3] was exploited for the microextraction of different classes of environmental pollutants among which PAHs and fragrance materials at trace levels. The unique properties in terms of area-to-volume ratio, surface interaction tunability and affinity towards the target analytes allowed to achieve enhanced extraction capability with enrichment factors up to 15 times higher than commercially available materials. Detection limits in the low ng/L range were obtained, thus assessing the reliability of the developed methods for the analysis of real samples at ultratrace levels.

[1] F. Bianchi, S. Agazzi, N. Riboni, N. Erdal, M. Hakkarainen, L.L. Ilag, L. Anzillotti, R. Andreoli, F. Marezza, F. Moroni, R. Cecchi, M. Careri, *Talanta* **2019**, *202,* 136-144

[2] N. Riboni, J. Trzcinski, F. Bianchi, C. Massera, R. Pinalli, L. Sidisky, E. Dalcanale, M. Careri, *Anal. Chim. Acta* **2016**, *905*, 90579-84

[3] D. Balestri, P. P. Mazzeo, R. Perrone, F. Fornari, F. Bianchi, M. Careri, A. Bacchi, P. Pelagatti, *Angew. Chem. Int. Ed.* **2021**, *60*, 10194-10202

Secondary reactions in the analysis of microplastics by Py-GC-MS

Irene Corralli[a], Valerio Giorgi[b], Alessandro G.Rombolà[a], Ivano Vassura[bc,] Daniele Fabbri[ac]*

[a] Department of Chemistry "Giacomo Ciamician" c/o Tecnopolo di Rimini, University of Bologna, via Dario Campana 71 47192 Rimini (Italy); [b] Department of Industrial Chemistry ''Toso Montanari", University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy ;[c] Interdepartmental Center for Industrial Research FRAME and MAM, Via Dario Campana 71, 47921 Rimini, Italy

Over the last decade, environmental pollution caused by microplastics (MP) has become of emerging concern, attracting worldwide attention. Py-GC-MS is acquiring increasing importance in the analysis of MP because it can provide information about the chemical nature of polymers with no restrictions on the size and the shape of the sample. Moreover, it is selective and capable to provide mass-based quantitative data [1,2]. However, a deep knowledge of the pyrolytic behaviour of polymers in mixtures is required in order to recognise potential artefacts. Recent studies have highlighted that secondary reactions can occur between some polymers affecting their correct quantification [3]. This contribution aimed at providing further information on this topic. MP from seven common polymers (PE, PP, PS, PVC, PET, PA6 and PA66) were analysed as single polymers and their mixtures by Py-GC-MS at 500 °C. The pyrograms of mixtures showed dissimilarities from the superimposition of the pyrograms of single polymers. The most noticeable difference was the appearance of new peaks that were attributed to secondary reactions between PET and PA (aromatic nitriles) and PVC (chlorinated benzoic acid derivatives). The identity and mechanism of formation of pyrolysis products was investigated by co-pyrolysis of PET with PA6, PA66 and PVC particles. The pyrolytic behaviour of model compounds was also investigated (e.g. (alkyl)ammonium salts of benzoic acid). Quantitative Py-GC-MS analysis of MP mixtures was based on typical pyrolytic markers of each polymer. Results were satisfactory for polyolefins, but not for PET and PA6 probably due to secondary reactions. Quantitation of these latter polymers was improved under methylating conditions (thermally assisted hydrolysis and methylation with TMAH), even though pyrolysis products from secondary reactions were not totally eliminated.

[1] M. Fischer, B.M. Scholz- Böttcher, *Environ. Sci. Technol.,* **2017**, *51*, 5022-2060.
[2] M. Fischer, B.M. Scholz- Böttcher, *Environ. Sci. Technol.,* **2019**, *11*, 2489-2497.
[3] M. Matsueda et al., *J. Anal. Appl. Pyrolysis,* **2021**, *154*, 104993.

Investigation of the chemoselectivity of normal phase stationary phases towards the separation of cannabinoids

S. Felletti [a]*, *A. Buratti* [a], *C. De Luca* [a], *F. Pellati* [b], *V. Brighenti* [b], *Y. Krauke* [c], *S. Stephan* [c], *K. Monks* [c], *M. Catani* [a], *A. Cavazzini* [a]

[a] *Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, via Borsari 46, 44121, Ferrara, Italy;* [b] *Department of Life Sciences, University of Modena and Reggio Emilia, Via G. Campi 103, 41125 Modena, Italy;* [c] *KNAUER Wissenschaftliche Geräte GmbH, Hegauer Weg 38, 14163 Berlin*

Due to the progress decriminalization of recreational cannabis and the growing interest in hemp and cannabis products, in the last years much effort has been devoted to investigating the biological and pharmacological activity of cannabinoids in order to ensure consumer safety [1]. However, only 20% of natural occurring cannabinoids (or phytocannabinoids) is currently available as a certified reference material and new cannabinoids are continuously being discovered [2].

The purification of cannabinoids, especially from hemp extracts, could be very challenging due to the presence of a large number of components (such as terpenes, waxes, other cannabinoids, etc.), many of them with similar chemical structure. This points the attention on the need of fast, efficient and cost-effective methods for the isolation and purification of cannabinoids, especially from plant materials [3,4].

In this field, preparative liquid chromatography (LC) and multicolumn countercurrent chromatography (MCC) are the most employed technique for industrial purification of cannabinoids. However, a deeper understanding of the fundamentals of cannabinoids retention is required for the selection of the optimal combination of mobile phases and column chemistries.

In this work, the effect of the stationary phase polarity on retention, separation and selectivity of five different neutral phytocannabinoids, namely CBD, CBC, CBG, CBN and Δ^9-THC, has been investigated on four 150×4 mm polar columns packed with 5 μm particles under normal phase (NP) isocratic elution conditions.

Results, obtained in an analytical scale, indicate that NP chromatography could be very promising if applied to large scale separations and purifications of cannabinoids, when compared to RP chromatography, due to fast analysis, low backpressure, high selectivity and high sample solubility.

References

[1] E. M. Williamson, F. J. Evans, *Drugs* **2000**, *60*, 1303–1314.

[2] C. Citti, P. Linciano, F. Russo, L. Luongo, M. Iannotta, S. Maione, A. Laganà, A. L. Capriotti, F. Forni, M. A. Vandelli, G. Gigli, G. Cannazza, *Sci Rep*. **2019**, *9*, 20335.

[3] C. Citti, P. Linciano, F. Forni, M. A. Vandelli, G. Gigli, A. Laganà, G. Cannazza, *J. Pharm. Biomed. Anal.* **2019**, *175*, 112752.

[4] S. Felletti, Y. Krauke, S. Stephan, K. Monks, *App. Note* **2021**, VFD0189

Potential Health Impact Assessment of New Pocket Pen-Vaporizers: Vapor Characterization Using SPME-GC/MS

Giuseppina Gullifa [a], Laura Barone [a], Roberta Risoluti [a]

[a] Department of Chemistry, Sapienza - University of Rome, P.le A. Moro 5-00185 Rome, Italy;

Everyone knows that smoking is the main cause of lung damage, yet many people persist in smoking. The new emerging electronic delivery systems (EDS) appear less harmful then mainstream cigarettes. EDS work by heating of a liquid solution or dry material leading to assumption of their constituents by inhalation of an aerosol.

In recent years, in addition to electronic cigarettes (e-cigarettes or e-cigs), e-cigars, e-pipes and e-hookahs, that are the electronic nicotine delivery systems (ENDS) commonly used to vape, vaporizers for “cannavaping” have been interested by a rapid evolution and diffusion. Tabletop or personal portable vaporizers have obtained particular attention in the emerging hemp industry thanks to their capability to volatilize the active ingredients (phytocannabinoids, flavonoids, and terpenoids) from heat dried cannabis without production of combustion by-products. However, vaporizers safety is still controversial and their increasing popularity requires further investigation on the potential health risks/benefits.

In this study, the characterization of vapor phase produced by cannavaping was performed in order to assess potential health impacts relating to the new pocket pen-vaporizers use. For achieving this object, vaping was performed under standard conditions and vapor phase was collected in quick and direct manner in order to avoid any degradation and contamination. Solid Phase Microextraction (SPME) was carried out to isolate analytes developed during vaping and their identification and determination were accomplished by gas chromatography coupled with mass spectrometry (GC/MS). The optimized SPME-GC/MS method allowed to monitor active ingredients and to verify the presence or absence of harmful compounds which characterize the mainstream cigarette smoke. Based on the identified compounds, the potential impact of the novel investigated vaporizers for human health was evaluated. The possibility of heating the entire plant, releasing cannabinoids and terpenes in a vapor that is relatively free from the by-products of combustion would make the emerging pocket-pen vaporizers a promising commercial product for hemp industry and a valuable tool for cannabinoids administration in medicine.

[1] A. B. Stefaniak, R. F. LeBouf, A. C. Ranpara, S. S. Leonard, *Pharmacol. Ther.* **2021**, 224, 107838

Analytical pyrolysis coupled with gas chromatography/mass spectrometry and solvent extraction for the characterization of microplastics and polymer additives

Jacopo La Nasa, Greta Biale, Marco Mattonai, Valter Castelvetro, Andrea Corti, Francesca Modugno

Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa

Sampling, separation, detection and characterization of micro- and nano-plastic pollutants is a challenging and critical goal, fundamental to assess their amount, fate, and the related hazards for ecosystems. While an increasingly large number of studies are focused on determining the distribution and concentration of plastic microparticles in different environmental compartments, there is still a major lack of understanding of the most relevant mechanisms of interaction and exchange of this class of pollutants with the environment and with organisms. Analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS) has been demonstrated a powerful tool for the unambiguous identification of microplastics [1], however the potential to investigate microplastic degradation processes is unexplored. We combined different approaches based on analytical pyrolysis for the characterization of microplastics and their solvent extractable fractions deriving from photo-oxidative degradation. This set of analytical techniques was initially tested, optimized, and validated on artificially aged reference polymers (polypropylene, polystyrene, high- and low-density polyethylene, polyethylene terephthalate), and then applied to degraded plastic debris collected in shore-line environment [2]. Samples of micronized reference polymers were photoaged and investigated at different aging times. The aged polymers were extracted with solvents in conditions specifically optimized to selectively extract the degraded (oxidized) fractions produced during irradiation. We applied evolved gas analysis/mass spectrometry (EGA), Py-GC-MS, and cryo-focusing chromatographic methods to characterize the bulk polymers at different ageing times, the extractable fractions, and the corresponding extraction residues [3]. The analysis performed on the extracts and the extraction residues allowed us to gain information on the products of oxidation/fragmentation and on the complex microplastics degradation processes, such as the formation of short chain carboxylic acids from polypropylene and of long chain carboxylic acids from polyethylene. EGA-MS allowed us to distinguish the different polymer fractions based on their specific degradation temperatures: the data obtained with this approach were used to set-up and optimize the Py-GC/MS experiments. The combination of extraction procedures and the analytical approaches based on pyrolysis achieved significant information for a better understanding of the chemical nature of degradation products potentially released by the different polymers present as microplastics in the environment

[1] J. La Nasa, G. Biale, D. Fabbri, F. Modugno, "A review on challenges and developments of analytical pyrolysis and other thermoanalytical techniques for the quali-quantitative determination of microplastics", *Journal of Analytical and Applied Pyrolysis*, **2020**, vol.149, 104841; N. Yakovenko, A. Carvalho, A. ter Halle, "Emerging use thermo-analytical method coupled with mass spectrometry for the quantification of micro(nano)plastics in environmental samples", *Trends in Analytical Chemistry*, **2020**, vol. 131, 115979.
[2] J. La Nasa, G. Biale, M. Mattonai, F. Modugno, "Microwave-assisted solvent extraction and double-shot analytical pyrolysis for the quali-quantitation of plasticizers and microplastics in beach samples", *Journal of Hazardous Materials*, **2021**, vol. 401, 123287.
[3] G. Biale, J. La Nasa, M. Mattonai, A. Corti, V. Vinciguerra, V. Castelvetro, F. Modugno, "A systematic study on the degradation products generated from artificially aged microplastics", **2021** *submitted.*

Evaluation of carbon - clad zirconia columns as stationary phases for superheated water liquid chromatography

Roberta La Tella[a], Francesca Rigano[a], Luigi Mondello[a,b,c,d]

[a]*Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

[b]*Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

[c]*Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy*

[d]*BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

The present research focuses on the use of high temperatures to achieve fast separations in Liquid Chromatography (LC), minimizing the percentages of organic solvents. Particularly, superheated water was employed, by exploiting the decrease in dielectric constant of water by increasing temperature [1]. In order to realize this kind of application, the availability of LC column resistant at high temperature is mandatory. In this work, the performances of a carbon-clad zirconia (ZR) phase with covalently bonded octadecyl group was evaluated, in terms of robustness, efficiency and resolution. An HPLC system was interfaced to a GC oven, which hosts the LC column; in order to achieve a fast and efficient heating of the eluent coming from the autosampler prior to enter into the column, a pre-heating tube was interposed between the autosampler outlet and the column inlet. Instead, a cooling loop is connected to the column outlet to cool the LC effluent prior to enter into the UV detector. A mixture of parabens was used to perform a fundamental study, by evaluating the performance of the column at different temperatures, organic solvent percentages and flow rates.

[1] P. Dugo, K. Buonasera, M.L.Crupi, F. Cacciola, G. Dugo, L. Mondello, *J. Sep. Sci.* **2007**, *30*, 1125-1130

Fabric Phase Sorptive Extraction: an innovative tool for TDM and pharmacotoxicological studies using unconventional biological matrices

M. Locatelli[a], *A. Kabir*[b], *H.I. Ulusoy*[c], *G.M. Merone*[d], *F. Savini*[d], *C. D'Ovidio*[e], *M. Bonelli*[e], *E. Rosato*[a], *U. De Grazia*[f], *K.G. Furton*[b], *A. Tartaglia*[a]

(a) Department of Pharmacy, University of Chieti–Pescara "G. d'Annunzio", Via dei Vestini 31, Chieti 66100, Italy; (b) Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th St, Miami, FL 33199, USA; (c) Department of Analytical Chemistry, Faculty of Pharmacy, Cumhuriyet University, Sivas 58140, Turkey; (d) Pharmatoxicology Laboratory—Hospital "Santo Spirito", Via Fonte Romana 8, Pescara 65124, Italy; (e) Department of Medicine and Aging Sciences, Section of Legal Medicine, University of Chieti–Pescara "G. d'Annunzio", Chieti 66100, Italy; (f) Fondazione IRCCS Istituto Neurologico Carlo Besta, Laboratory of Neurological Biochemistry and Neuropharmacology, Via Celoria 11, Milan 20133, Italy

Sample preparation has been recognized as a major step in the chemical analysis workflow. As such, substantial efforts have been invested in recent years to simplify the overall sample preparation process. Major focusses of these efforts include, miniaturization of the extraction device; minimizing/eliminating toxic and hazardous organic solvent consumption; eliminating sample pre-treatment and post-treatment steps; reducing the sample volume requirement; reducing extraction equilibrium time, maximizing extraction efficiency etc.

The extreme complexity of biological samples such as whole blood, plasma, serum, urine, and saliva demands a simple, fast and robust sample preparation process prior to the instrumental analysis. Conventional sorbent-based sample preparation techniques including solid phase extraction and its different modifications often involve protein precipitation, solvent evaporation and sample reconstitution as the integral part of sample preparation workflow. These extra steps are time consuming and may lead to substantial analyte loss. In order to eliminate these steps from the sample preparation workflow, in this presentation we will report the latest and innovative application of fabric phase sorptive extraction (FPSE) to small drugs analyses in different biological matrices like whole blood, plasma, urine, saliva, exhaled breath aerosol [1-3] with primary emphasis on unconventional sample matrix such as saliva due to its easy and non-invasive collection potential.

[1] A. Kabir, K.G. Furton, N. Tinari, L. Grossi, D. Innosa, D. Macerola, A. Tartaglia, V. Di Donato, C. D'Ovidio, M. Locatelli, Fabric Phase Sorptive Extraction-High Performance Liquid Chromatography-Photo Diode Array Detection Method for Simultaneous Monitoring of Three Inflammatory Bowel Disease Treatment Drugs in Whole Blood, Plasma and Urine, J. Chromatogr. B 1084 (2018) 53-63.
[2] A. Tartaglia, A. Kabir, F. D'Ambrosio, P. Ramundo, S. Ulusoy, H.I. Ulusoy, G.M. Merone, F. Savini, C. D'Ovidio, U. De Grazia, K.G. Furton, M. Locatelli, Fast *off-line* FPSE-HPLC-PDA determination of six NSAIDs in saliva samples, J. Chromatogr. B 1144 (2020) article 122082, 1-9.
[3] M. Locatelli, A. Tartaglia, H.I. Ulusoy, S. Ulusoy, F. Savini, S. Rossi, F. Santavenere, G.M. Merone, E. Bassotti, C. D'Ovidio, E. Rosato, K.G. Furton, A. Kabir, Fabric phase sorptive membrane array as non-invasive in vivo sampling device for human exposure to different compounds, Anal. Chem. 93(4) (2021) 1957-1961, doi: 10.1021/acs.analchem.0c04663.

Molecular imprinted polymer coupled to LC-MS/MS for maleic hydrazide determination in food samples

Sara Palmieri, Dounia ElFadil, Flavio Della Pelle, Manuel Sergi, Dario Compagnone

Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, 64100, Teramo,

Maleic hydrazide (MH) is a plant growth regulator, herbicide, and sprout inhibitor widely used in crops. The MH is widely used to 'control' ripening and storage stages in particular for potatoes, onions, garlic, and also tobacco [1]. The determination and monitoring of MH residue in foods result crucial since its assumption can lead to adverse effects on health and also for economic reasons [2]. In literature are reported different methods for the determination of the MH, such as HPLC and electrochemical analysis, however, the critical issue in the MH selective extraction [3,4]. Indeed, the high polarity of MH does not allow conventional extraction and clean-up procedures, for this reason, the search for selective extraction strategies for MH result still a challenge.

In this work is presented a new molecularly imprinted polymer (MIP) able to act as a selective extraction sorbent phase for MH. The selected MIP was synthesized by bulk polymerization, using methacrylic acid (MAA), ethylene glycol (EGDMA), and azobisisobutyronitrile (AIBN) as functional monomer, cross-linker, and free radical initiator, respectively. Logically MH was used as the template molecule.

The sorbent ability of MIPs was proved towards MH extraction in model solutions, demonstrating useful binding ability and outstanding selectivity, allowing MH extraction in polar solutions. On-course tests are devoted to optimizing SPE-based extraction procedures, to selective isolate MH from complex food matrices. To the best of our knowledge, extraction of MH is possible only by using cumbersome and time spending procedures, our preliminary results make us confident to affirm that the here presented MIP can represent an effective and smart solution to MH selective extraction from complex matrices.

[1] Abdelwahed, M. H., Khorshed, M. A., Elmarsafy, A. M., Elshabrawy, M. S., & Souaya, E. R., *Food Analytical Methods*. **2021**, 14(1), 172-185.
[2] Ponnampalam, R., Mondy, N. I., & Babish, J. G., R*egulatory Toxicology and Pharmacology*. **1983**, 3(1), 38-47.
[3] Arribas, A. S., Bermejo, E., Chicharro, M., & Zapardiel, A., *Talanta.* 2007, 71(1), 430-436.
[4] Chamkasem, N., *Journal of agricultural and food chemistry*. **2017,** 65(34), 7535-7541.

Determination of lactose in low-lactose milk by direct liquid injection and high-resolution mass spectrometry.

Marco Roverso[a], *Raghav Dogra*[a], *Giuseppe Di Bernardo*[a], *Gabriella Favaro*[a], *Paolo Pastore*[a], *Sara Bogialli*[a]

[a] *Department of Chemical Sciences, University of Padua, Via Marzolo 1, 35131 Padova, Italy.*

The marketing of lactose-free products is in constant growth, due to the increase of people affected by lactose intolerance. Therefore, sensitive, and accurate analytical methods for lactose quantification are needed in industrial quality control processes and to ensure the reliability of products to final consumers.

In this work, a novel and fast analytical method, based on flow injection analysis (FIA) coupled to high resolution tandem mass spectrometry (HR-MS/MS), was optimized, and validated for the quantitative determination of lactose in low-lactose and lactose free commercial milk.

Firstly, the development of the method was focused on the optimization of the electrospray (ESI) parameters (gas flow, temperatures, applied voltage) to maximize the ionization of the analyte.

Furthermore, the sample preparation procedure was maintained as simple as possible, by performing simple dilutions of the specimen with different solvents and modifiers (e.g., sodium formate). Extensive protein precipitation and lipid dilution was evaluated to maximize sensitivity and accuracy and to avoid the matrix effect. The selectivity of the method, in particular the discrimination of the presence of lactulose (an isobaric interferent originating from the lactose reducing process), was assessed by evaluating specific fragment ions for lactose in MS/MS mode.

The removal of the matrix effect and the accuracy of the optimized workflow were tested by comparing results from external calibration and standard additions methods. Furthermore, the performances of the analytical workflow were tested and validated on milk samples with variable fat content.

Concluding, the proposed method is suitable for an accurate and effective determination of lactose in low-lactose and lactose free milk with numerous advantages, such as short analysis time and simplified sample pretreatment, compared to methods based on chromatographic techniques, with comparable performances. A simple extraction with solvent and dilution of the sample guaranteed good sensitivity, limited matrix effects and satisfactory recovery and robustness. The specificity is comparable to enzymatic assays [1] and is independent from errors due to the presence of interferents, allowing great precision and high sensitivity.

Future research will provide further data on the validation of the method in other matrices, such as dairy products, food containing milk, preparations with lactose as an excipient, drugs and antibiotics.

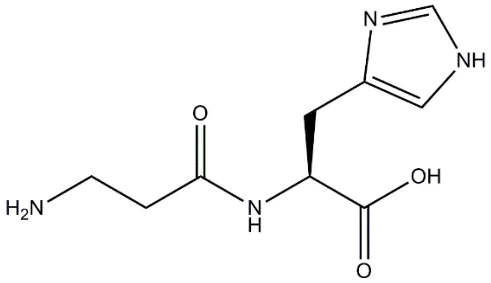
[1] A. Trani, G. Gambacorta, *et al., Food Chem*., **2017**, 233, 385.

Sequestering ability of carnosine towards some potentially toxic divalent metal cations in aqueous solution

Chiara Abate, Claudia Foti, Ottavia Giuffrè

Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Viale Ferdinando Stagno D'Alcontres, 31, 98166, Messina, Italy

Carnosine or β-Alanine-L-Histidine is a highly concentrated endogenous dipeptide in skeletal muscle and brain tissues.



β-Alanyl-L-Histidine (carnosine)

Carnosine has numerous ergogenic and therapeutic properties; for these reasons, its physiological role is still widely studied.[1] Potential biological roles include intracellular pH buffering, metal ion chelating capacity and antioxidant property.[2] In addition to its biochemical behavior and since carnosine can act as a chelating ligand, forming coordination complexes with different metal cations, we focus precisely on the possible interactions of carnosine with three specific ions, Cd^{2+}, Hg^{2+} and Pb^{2+}, to evaluate its potential employ in the removal of toxic metals from natural aqueous systems. For this purpose, a speciation study on carnosine-metal cation systems was performed as a starting point to assess its possible use in removing techniques.

The complexing ability of the ligand towards Cd^{2+}, Hg^{2+}, Pb^{2+}, was investigated by potentiometry in NaCl aqueous solution at different conditions of temperatures ($15 \leq t \leq 37$ °C) and ionic strengths ($0.1 \leq I \leq 1$ mol L^{-1}). Once the thermodynamic interaction parameters were defined, the sequestering capacity of carnosine towards metal cations was evaluated by the determination of an empirical parameter, $pL_{0.5}$, which represents the ligand concentration able to sequester 50% of the metal cation. The $pL_{0.5}$ values were determined under specific conditions of pH, temperature and ionic strength in order to establish the best conditions for the use of carnosine in the removal techniques. This considerably simplifies the experimental procedure for setting removal requirements.

On the basis of this quantitative study on the interactions between metal cations and ligand, preliminary tests are underway on adsorption materials functionalized with the carnosine.

[1] E. Dolana, B. Saundersa, R.C. Harrisc, J.E. Pereira, W. Bicudo, D.J. Bishope, C. Sale, B. Gualano, *Comparative Biochemistry and Phisiology, Part A.* **2019**, *234*, 77-86.
[2] K. Chmielewska, K. Dzierzbicka, I. Inkielewicz-Stępniak, M. Przybyłowska, *Chemical Research in Toxicology.* **2020**, *33*, 1561-1578.

Pb^{2+} ions adsorption onto bovine serum albumin-based aggregates: a kinetic and thermodynamic study

Sara Anselmo, Tiziana Avola, Salvatore Cataldo, Alberto Pettignano, Giuseppe Sancataldo, Valeria Vetri

Dipartimento di Fisica e Chimica - Emilio Segrè, Viale delle Scienze, Edificio 17, Università di Palermo, I-90128 Palermo, Italy

In this study, bovine serum albumin (BSA) aggregates have been used as adsorbent material for the removal of Pb^{2+} ions from aqueous solutions. Kinetic adsorption experiments were carried out in three different ionic media (NaCl and NaCl/$NaNO_3$ and $NaNO_3$) at fixed ionic strength (0.1 mol L^{-1}), pH ~ 5 and at $T = 298.15$ K. The dependence of the adsorption ability on ionic medium, pH and temperature have been evaluated carrying out batch isotherm experiments at different experimental conditions. Both kinetic and equilibrium experiments were carried out by using the differential pulse anodic stripping voltammetry (DP-ASV) technique to measure the metal ion concentration before and after contact with the adsorbent material. Different kinetic (pseudo-first order, pseudo-second order, pseudo generic order and double-exponential) and isotherm (Langmuir and Freundlich) models were used to fit experimental data.

The thermodynamic parameters (ΔG, ΔH and ΔS) of Pb^{2+} adsorption process were calculated by using Gibbs and van't Hoff equations. In order to test the reusability of the adsorbent material, four Pb^{2+} adsorption-desorption cycles were done in putting the BSA in a glass column and using a metal ion ($C_{Pb2+} \approx 30$ mg L^{-1}) solution at $I = 0.1$ mol L^{-1} ($NaNO_3$), pH ~ 5 and at $T = 298.15$ K and, as extracting solution, EDTA 0.1 mol L^{-1}.

The results showed that the BSA is a good adsorbent material of Pb^{2+} ions. The ionic medium, the ionic strength, the pH and the temperature affect the kinetic of adsorption as well as the adsorption capacity and affinity of BSA towards the metal ion.

The higher adsorption value was obtained at pH = 5.0, without ionic medium and at $T = 283.15$ K ($q_m = 211.3$ mg g^{-1}). An adsorption mechanism mainly based on ionic exchange has been hypothesized.

[1] V. Vetri, N. Foderà, *FEBS Letters* **2015**, 589 (19PartA), 2448.

[2] http://www.Rcsb.Org/Structure/3V03

Understanding the thermodynamics and coordination chemistry of metal-binding proteins: the common thread to elucidate metal acquisition processes at host/pathogen interface

Denise Bellotti,[a,b] *Magdalena Rowińska-Żyrek,*[b] *Maurizio Remelli* [a]

[a] *Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Italy;* [b] *Faculty of Chemistry, University of Wrocław, Poland*

Several studies have shown that the disruption of metal homeostasis in bacterial and fungal cells can be a powerful tool to design new antimicrobial drugs with a high rate of selectivity and specificity. To prevent infections, in fact, the human organism reduces the bioavailability of essential micronutrients by means of an innate immune response termed "nutritional immunity"; on the contrary, pathogens rely on specialized metal-binding proteins and molecular systems which capture the metal ions from the competitive host environment forming stable complexes [1]. Understanding the properties, structure and action mechanisms of the involved metal chelators is the very first step to elucidate the dynamics behind the metal transfer mechanisms and to rationally design novel metal-based antibiotic therapeutics [2].

An outstanding example is given by the thermodynamic and spectroscopic characterization of the zinc and copper binding sites of the periplasmic protein ZinT, expressed by *Escherichia coli* and *Salmonella enterica* [3, 4]. The chosen unstructured fragments, which serve as models to simulate the coordination and transport of metal ions in ZinT protein, correspond to the 24–29 and 166–178 amino acid sequences and are protected at their amino- and carboxyl-termini: Ac-^{24}HGHHSH^{29}-Am and Ac-^{166}DHIIAPRKSSHFH^{178}-Am (*E. coli*), Ac-^{24}HGHHAH^{29}-Am and Ac-^{166}DHIIAPRKSAHFH^{178}-Am (*S. enterica*).

A deep investigation on the thermodynamics and coordination chemistry of the formed Zn(II) and Cu(II) complexes was performed through different experimental techniques. The protonation and complex-formation equilibria were studied by means of potentiometric acid-base titrations. ESI mass spectra of the solutions under examination allowed to confirm the stoichiometries of the formed species and, through UV-Vis, CD and EPR spectroscopies at variable pH values, the metal coordination spheres and the geometry of the complexes were explored. Finally, the obtained results allowed a comparison with other biologically relevant metal-binding systems, such as the antimicrobial peptide calcitermin (VAIALKAAHYHTHKE) which can, in principle, participate in human nutritional immunity, competing with ZinT for the metal ion acquisition.

Financial support of the National Science Centre (UMO-2020/37/N/ST4/03165) is gratefully acknowledged. This paper is based upon work from COST Action CA18202, NECTAR – Network for Equilibria and Chemical Thermodynamics Advanced Research, supported by COST (European Cooperation in Science and Technology).

References

[1] D. A. Capdevila, K. A. Edmonds, D. P. Giedroc, *Essays Biochem.*, **2017**, *61*(2), 177-200.
[2] S. R. Hennigar, J. P. McClung, *Am. J. Lifestyle Med.*, **2016**, *10*(3), 170-173.
[3] A. Battistoni, A. Ammendola, E. Chiancone, A. Ilari, *Future Med. Chem.*, **2017**, *9*(9), 899-910.
[4] D. Bellotti, M. Rowińska-Żyrek, M. Remelli, *Dalton Trans.*, **2020**, *49*(27), 9393-9403.

Complex formation equilibria of a kojic acid derivative with different metal ions

R. Cappai [a], V. M. Nurchi [a], G. Crisponi [a], M. Peana [b], M. A. Zoroddu [b], A. Pelucelli [b], S. Medici [b], E. Garriba [b], V. Ugone [b], D. Sanna [b]

[a] *Dipartimento di Scienze della Vita e dell'Ambiente, Università di Cagliari*
[b] *Dipartimento di Chimica e Farmacia, Università di Sassari*

Several factors determine human exposure to toxic metal ions, mainly due to environmental and occupational causes, and including metal overload for genetic diseases (β-thalassaemia and Wilson's disease). Therapeutic detoxification, through complexation of the target metal ions by specific chelating agents, appears an efficacious strategy. In this regard, based on the previous studies of kojic acid (KA) derivatives, we synthetized 6,6′-(2-(diethylamino)ethylazanediyl)bis(methylene)bis(5-hydroxy-2-hydroxymethyl-4H-pyran-4-one) (L9), characterized by an amine-bearing bis-KA (Fig. 1). A variety of techniques, potentiometry, UV–Vis, NMR spectroscopy, EPR, ESI–MS, quantum mechanical calculations and X-ray diffraction have facilitated the characterization of the ligand, and the corresponding metal complexes, together with an exhaustive analysis of the protonation and complex equilibria. The coordination ability has been evaluated for several metal ions including Fe^{3+}, Al^{3+}, Cu^{2+} and Zn^{2+} and recently VO^{2+} [1-2].

We present herein the description of the results gained since now, which are fully informative of the affinity and selectivity of each metal ion investigated. Different coordination modes were identified and characterized. These were related to the peculiar chemical features of each metal ion, including the hard-soft character, the oxidation states and the ionic radius.

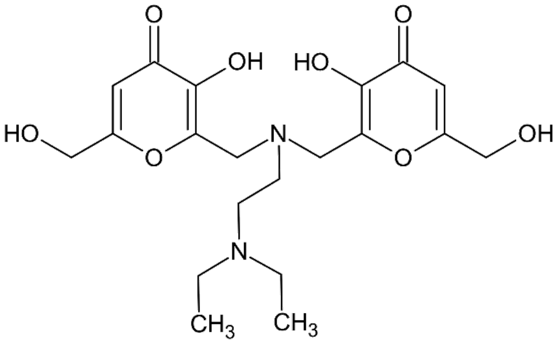


Figure 1. L9 structure

[1] V. M. Nurchi, G. Crisponi, M. Arca, M. Crespo-Alonso, J. I. Lachowicz, D. Mansoori, L. Toso, G. Pichiri, M. A. Santos, S. M. Marques, J. Niclòs-Gutierrez, J. P. Gonzaléz-Pérez, A. Domìnguez-Martìn, D. Choquesillo-Lazarte, Z. Szewczuk, M. A. Zoroddu, M. Peana, *J. Inorg. Biochem*. **2014**, *141*, 132-143.

[2] M. Peana, S. Medici, V. M. Nurchi, J. I. Lachowicz, G. Crisponi, M. Crespo-Alonso, M. A. Santos, M. A. Zoroddu, *J. Inorg. Biochem*. **2015**, *148*, 69-67.

CYCLODEXTRIN-BASED NANOSPONGES FOR LEAD(II) ION ADSORPTION FROM AQUEOUS SOLUTIONS

Salvatore CATALDO, [a] *Paolo LO MEO,* [b] *Pellegrino CONTE,* [c] *Antonella DI VINCENZO,* [b]
Demetrio MILEA, [d] *Alberto PETTIGNANO,* [a]

[a] *Dipartimento di Fisica e Chimica – Emilio Segrè, Università di Palermo, V.le delle Scienze Ed.17, 90128, Palermo, Italy;* [b] *Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche (STEBICEF), Università di Palermo, V.le delle Scienze, Ed.17, 90128, Palermo, Italy;* [c] *Dipartimento di Scienze Agrarie, Alimentari e Forestali, Università di Palermo, V.le delle Scienze, Ed.4, 90128, Palermo, Italy;* [d] *Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina, V.le F. Stagno d'Alcontres, 31, 98166 Messina, Italy.*

Sorbent materials capable to remove both inorganic and organic species are valuable tools for designing environmental remediation devices for the treatment of polluted waters.

Recently, an increasing attention has been paid to composite materials based on cyclodextrins (CDs) [1]. They can be considered a sustainable material being obtained via bacterial digestion of starch. They are highly functionalized molecules, with a great number of primary and secondary hydroxyl groups liable to undergo chemical transformation by quite simple organic reaction routes [2].

The reaction between CDs and suitable reticulating agents allows accessing to a further class of sorbent materials, namely Nanosponges (NSs) [3]. NSs show a great permeability to aqueous media a good swellability and maintain the inclusion ability of CDs [4].

Due to their characteristics, NSs have many applications: drug carrier/delivery, devices to sensors, environment remediation, active packaging [5,6].

Here, several pristine and chemically post-modified cyclodextrin - calixarene nanosponges (CyCaNSs) have been synthesized. Four kind of CyCaNSs were chosen and used as adsorbent materials to remove Pb^{2+} ions from aqueous solutions. The adsorbent materials were characterized by means of FFC-NMR relaxometric techniques [7].

In order to simulate the real polluted water systems, the adsorption tests were performed under different operational conditions. The experiments were carried out on solutions without and with the addition of background salts, at different pH, ionic strengths and temperatures. $NaNO_3$ and NaCl were used, changing the ionic strength in the range 0.01 - 0.10 mol L^{-1}. The initial pH was fixed at 3.0 and 5.0, while the effect of temperature was studied in the range 283.15 - 323.15 K. The adsorption capacity of the nanosponges towards Pb^{2+} ions were kinetically and thermodynamically investigated by measuring the metal ion concentration in the water samples of batch experiments by means of Inductively Coupled Plasma Emission Spectroscopy (ICP-OES) and Differential Pulse Anodic Stripping Voltammetry (DP-ASV). The acid-base properties of nanosponges and of metal ion as well as their interactions with the other interacting components of the systems have been considered in the evaluation of adsorption mechanism. To evaluate a possible recycling and reuse of the adsorbent materials, some specific experiments were carried out.

[1] A. H. Karoyo, L. D. Wilson, *Nanomaterials* **2015**, 5(2), 981.
[2] J. Szejtli, *Chem. Rev.* **1998**, *98(5)*, 1743.
[3] F. Caldera, M. Tannus, R. Cavalli, M. Zanetti, F. Trotta, *Int J of Pharm*. 2017, 531(2), 470.
[4] P. Lo Meo, F. Mundo, S. Terranova, P. Conte, D. Chillura Martino, *J Phys Chem B*. 2020, 124(9), 1847.
[5] R. Cavalli, F. Trotta, W. Tumiatti, *J. Incl. Phenom. Macro.* **2006**, *56(1-2)*, 209.
[6] S. Subramanian, S. Anandam, K. Kannan, M. Rajappan, *J. Pharm. Sci.* **2012**, *15*, 103.
[7] S. Cataldo, P. Lo Meo, P. Conte, A. Di Vincenzo, D. Milea, A. Pettignano, *Carbohyd. Polym.* **2021**, *267(1)*, 118151.

O-phosphorylethanolamine and O-phosphorylcholine in aqueous solution: acid-base behavior and speciation with Mg^{2+}

Ottavia Giuffrè,[a] Donatella Aiello,[b] Massimiliano Cordaro,[a] Claudia Foti,[a] Anna Napoli[b]

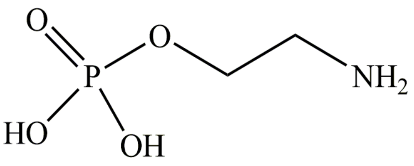
[a] Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina; [b] Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 87036 Arcavacata di Rende (CS).

O-phosphorylethanolamine (*PEA*) and O-phosphorylcholine (PPC) represent model compounds for the two most common headgroups of phospholipids. O-phosphorylethanolamine, a precursor of phosphatidylethanolamine, is present in all animal organs and tissues. It is associated with various phases of cell metabolism, such as hormone synthesis, mitochondrial metabolism and acetylcholine synthesis. The knowledge of their acid-base behaviors and complexing abilities towards metal cations of biological relevance represent a crucial issue. Among the essential metals, magnesium performs many important biochemical functions. One of its most important functions is to form complexes with phospholipids that stabilize membranes.

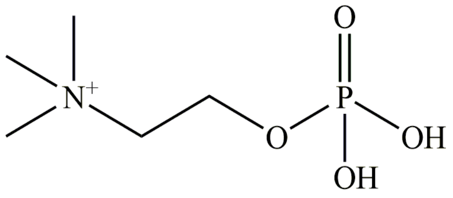
In this context, first the protonation constants of *PEA* and *PPC* were determined by potentiometric titrations in NaCl aqueous solutions at various ionic strengths ($0.15 \leq I$ / mol $L^{-1} \leq 1$) and temperatures ($15 \leq t$ / °C ≤ 37). A complexation study was then conducted for each of these ligands in the presence of Mg^{2+} under the same experimental conditions of the protonation measurements. The results showed the formation of three species for the system containing *PEA*, namely MLH_2, MLH and ML and two species for the one containing *PPC*, namely MLH and ML.

Based on the dependence of formation constants on the temperature, the enthalpy changes were determined for all the species at $t = 25$°C and $I = 0.15$ mol L^{-1}. As expected for hard-hard interactions, the species formed were mainly of electrostatic nature, where the standard free energy change is dominated by the entropic contribution. ^{1}H-NMR titrations were performed on both ligand and metal-ligand solutions at $t = 25$°C and $I = 0.15$ mol L^{-1}. The speciation model, the values of the ligand protonation and complex formation constants are in accordance with the potentiometric data under the same experimental conditions.

MALDI mass spectrometry on Mg^{2+}-PEA and Mg^{2+}-PPC solutions was also performed for the characterization of the complexes, as already done for other systems [1].



O-phosphorylethanolamine (**PEA**)



O-phosphorylcholine (**PPC**)

[1] D. Aiello D, F. Carnamucio, M. Cordaro, C. Foti, A. Napoli, O. Giuffrè, *Front. Chem.*, **2021**, *9*, 640219.

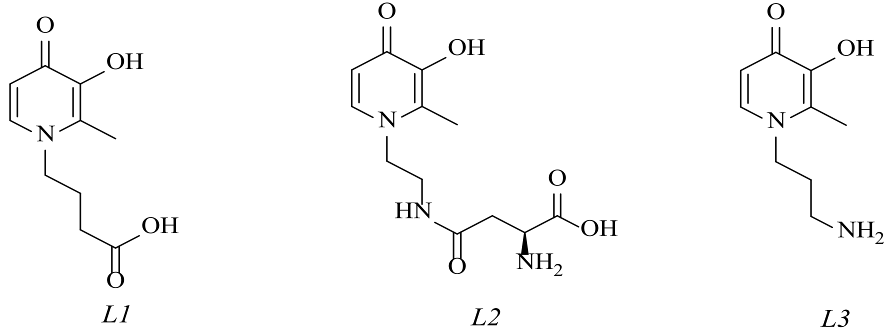
Thermodynamic parameters on the interaction of divalent and trivalent metal cations with 3-hydroxy-4-pyridinones

Anna IRTO,[a] *Paola CARDIANO,*[a] *Karam CHAND,*[b] *Rosalia Maria CIGALA,*[a] *Francesco CREA,*[a] *Concetta DE STEFANO,*[a] *Maria Amélia SANTOS*[b]

[a] *Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università di Messina, Viale F. Stagno d'Alcontres, 31 – 98166 Messina, Italy;* [b] *Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovísco Pais 1, 1049-001 Lisboa, Portugal*

The 3-hydroxy-4-pyridinones (3,4-HPs) are a family of compounds suitable for selective chelation of *hard* metal cations like Al^{3+} and Fe^{3+}. They are considered a good alternative to the use of deferoxamine as iron-decorporating drug because of their efficacy in all the biological conditions, without involving relevant side effects. These ligands are derivatives of deferiprone and consist of an aromatoid *N*-heterocyclic ring with a -OH and a ketone group in *ortho* position [1,2]. The 3,4-HPs can be easily N-extrafunctionalized to improve their metal chelating affinity and to modulate the pharmacokinetic properties and the potential interaction with proteins.

This contribution focuses on the results of an investigation on the interaction of three bifunctional 3-hydroxy-4-pyridinones with Cu^{2+} and Fe^{3+}, *borderline* and *hard* metal cations, respectively. The studies were performed at I = 0.15 mol L^{-1} in $NaCl_{(aq)}$ and T = 298.15 K using potentiometric and UV-Vis spectrophotometric techniques. The ligands (Figure 1) differ from each other for the presence of carboxylic and/or amino groups in their structures. The synthetic mechanisms used to prepare the 3,4-HPs and their acid-base properties have been already published in literature [2-4].



L1 *L2* *L3*

Figure 1. Structures of the 3-hydroxy-4-pyridinones under study.

The processing of the experimental data allowed the determination of speciation models featured by complexes with various stoichiometry and stability, due to the different functional groups present in the ligands structures, which could potentially participate to the metal complexation, and to the Cu^{2+} and Fe^{3+} behaviour in NaCl aqueous solution [5]. The sequestering ability of the 3-hydroxy-4-pyridinones towards the selected metal cations was also assessed by the calculation of empirical parameter $pL_{0.5}$ which represents the total concentration of ligand required to sequester the 50% of the metal cation present in trace in solution [6]. Finally, a comparison of the thermodynamic data determined for the Cu^{2+} and Fe^{3+}/3-hydroxy-4-pyridinones systems with the results already reported in literature [2, 7] for the same ligands with Zn^{2+} and Al^{3+}, also featured by *borderline* and *hard* character, respectively, appeared as a quite relevant issue.

[1] M.A. Santos, S. Chaves, *Future Med. Chem*. **2015**, *7* (3) 383-410.
[2] A. Irto, P. Cardiano, K. Chand, R. M. Cigala, F. Crea, C. De Stefano, L. Gano, S. Sammartano, M.A. Santos, *J. Inorg. Biochem*. **2018**, *185*, 116-129.
[3] M.A. Santos, M. Gil, S. Marques, L. Gano, G. Cantinho, S. Chaves, *J. Inorg. Biochem.* **2002**, *92*, 43-54.

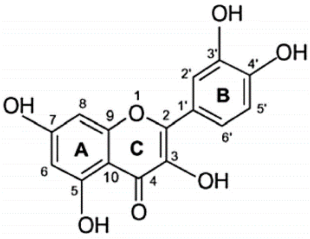
[4] M.A. Santos, R. Grazina, A.Q. Neto, G. Cantinho, L. Gano, L. Patrıcio, *J. Inorg. Biochem.* **2000**, *304*, 303-311.
[5] C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations. John Wyley & Sons, New York, **1976**.
[6] F. Crea, C. De Stefano, C. Foti, D. Milea, S. Sammartano, *Curr. Med. Chem.* **2014**, 21, 3819-3836.
[7] A. Irto, P. Cardiano, S. Cataldo, K. Chand, R.M. Cigala, F. Crea, C. De Stefano, G. Gattuso, N. Muratore, A. Pettignano, S. Sammartano, M.A. Santos, *Molecules* **2019**, 24, 4084.

Studies on the complexation between quercetin and some first-row transition metal cations in aqueous solution

Luana Malacaria, Emilia Furia

Department of Chemistry and Chemical Technologies, University of Calabria, 87036 Rende (CS)

Several investigations have demonstrated that the coordination of a drug with metal cations improves its pharmacological activity. Indeed, it is well known that chelation therapy is a promising method for the treatment of pathological diseases arising from oxidative stress caused by excess or dysregulation of transition metals [1-3]. In this context, flavonoids could complex several toxic metal ions, and for this reason have attracted the interest of researchers, also in consideration of their antibiotic, anticoagulant, anticancer and anti-inflammatory properties [4,5]. Recently, we have reported the complexation of quercetin (3,3′,4′,5,7-pentahydroxyflavone, H_5Que, Scheme 1) with Al(III), Fe(III) and Cu(II) in aqueous solutions at 37 °C and in 0.16 M NaCl, to evaluate the selectivity of this ligand towards bioavailable metal cations [6].



Scheme 1. Chemical structure of quercetin, H_5Que.

Quercetin is one of the most common flavonols in nature and is one of the most biologically active and common dietary flavonoid in fruits and vegetables. It may chelate metal cations, preventing the generation of damaging oxidizing radicals whose formation is mediated by metals and thus protecting the biological targets against oxidative stress [7]. Herein we introduce a study on the complexation ability of quercetin towards Cr(III), Co(II), Ni(II) and Zn(II) at 37° C and in 0.16 M NaCl, evaluating the stoichiometric composition and the corresponding stability constants of the complexes. The investigated equilibrium can be expressed according to the following general equation:

$$pM^{n+} + qOH^{-} + rL^{-} \rightleftarrows M_p(OH)_q(L)_r^{(np-q-r)+} \qquad \log \beta_{p,q,r}$$

Speciation profiles obtained by potentiometric titrations and supported by UV–Vis data show that in aqueous solution a complexation occurs at 1:1 and 2:1 ligand-to-cations ratio for Cr(III), Co(II) and Zn(II) and at 1:1 ligand-to-Ni(II) ratio.

[1] J. Kim, H.J. Lee, K.W. Lee, *J. Neurochem.* **2010**, *112*, 1415-1430.
[2] G. Crisponi, V.M. Nurchi, V. Bertolasi, M. Remelli, G. Faa, *Coord. Chem. Rev.* **2012**, *256*, 89-104.
[3] C. Exley, *J. Alzheimer Dis. Rep.* **2017**, *1*, 23-25.
[4] S. Selvaraj, S. Krishnaswamy, V. Devashya, S. Sethuraman, U.M. Krishnan, *Med. Res. Rev.* **2014**, *34*, 677–702.
[5] M. Kasprzak, A. Erxleben, J. Ochocki, *RSC Adv.* **2015**, *5*, 45853–45877.
[6] G.A. Corrente, L. Malacaria, A. Beneduci, E. Furia, T. Marino, G. Mazzone, *J. Mol. Liq.* **2021**, *325*, 115171–115182.
[7] L. Malacaria, G.A. Corrente, A. Beneduci, E. Furia, T. Marino, G. Mazzone, *Molecules* **2021**, *26*, 2603, 1-27.

Recognition of antibiotics by calixarene-based micellar aggregates in aqueous solution: binding features and driving forces

Rossella Migliore,[a] Giuseppe Granata,[a] Andrea Rivoli,[b] Grazia Maria Letizia Consoli,[a] Carmelo Sgarlata[b]

[a] Istituto di Chimica Biomolecolare, Consiglio Nazionale delle Ricerche (CNR), Via Paolo Gaifami 18, 95126, Catania, Italy; [b] Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale Andrea Doria 6, 95125, Catania, Italy

The search for novel drug delivery systems (DDSs) able to improve the performance of old-generation antibiotics is a topic of great interest due to overcoming problems associated with antibiotic resistance [1].

Polycationic calixarene derivatives able to self-assemble in nanoaggregates are promising novel nanocontainers for delivering antibiotics to bacteria due to their ability to establish electrostatic interactions with the negatively charged bacterial membranes [2]. In particular, a polycationic amphiphilic calix[4]arene, bearing choline groups and dodecyl aliphatic chains at the cavity upper and lower rim respectively, proved to be a promising nanocarrier for drug delivery [3].

The determination of the strength and nature of drug-micelle interactions is crucial for the design of novel medicines and the modification or selection of suitable shuttles for target-oriented drug delivery. However, despite the wide interest in the examination of these interactions, a quantitative analysis of the species, binding constants and thermodynamic parameters for the recognition/inclusion of a drug with(in) micellar assemblies has rarely been addressed.

The present work deals with the study of the binding features of polycationic calix[4]arene derivatives (CholineC4dod, MedeaC4dod and MedeaC4prop) with ofloxacin, chloramphenicol or tetracycline in neutral aqueous solution for investigating the capability of micellar aggregates to recognize and host three old generation antibiotics. These molecules were selected as models of antibiotics affected by the onset of resistance phenomena with the aim of contributing to the design and development of effective DDSs for the repurposing of old-fashioned drugs.

The study of the solution equilibria and the determination of the binding parameters in neutral aqueous solution were carried out using nano-isothermal titration calorimetry, that allows obtaining both stability constant and enthalpy change values for host-guest complex formation [4] and/or self-organization of surfactants into micelles by a single experiment [5,6].

ITC measurements showed that the formation of the chloramphenicol–micelle adduct is always an enthalpically driven process while the adducts with ofloxacin and tetracycline are always entropically driven and enthalpically unfavored. NMR experiments confirmed the picture on the positioning of the antibiotics within the micellar backbone provided by the ITC data [7].

[1] R. K. Kobayashi, G. Nakazato, *Front. Microbiol.* **2020**, *11*, 1421.

[2] I. Di Bari, R. Picciotto, G. Granata, A. R. Blanco, G. M. L. Consoli, S. Sortino, *Org. Biomol. Chem.* **2016**, *14*(34), 8047.

[3] G. Granata, S. Petralia, G. Forte, S. Conoci, G. M. L. Consoli, *Mater. Sci. Eng. C* **2020**, *111*, 110842.

[4] C. Bonaccorso, R. Migliore, M. A. Volkova, G. Arena, C. Sgarlata, *Thermochim. Acta* **2017**, *656*, 47.

[5] W. Loh, C. Brinatti, K. C. Tam, *Biochim. Biophys. Acta* **2016**, *1860*(5), 999.

[6] R. Migliore, *PhD Thesis*, University of Catania, **2019**.

[7] R. Migliore, G. Granata, A. Rivoli, G. M. L. Consoli, C. Sgarlata, *Front. Chem.* **2021**, *8*, 626467.

On-line ion trapping by frontal chromatography ICP-MS: a low-cost strategy for the fast speciation of inorganic pollutants

Davide Spanu[a], *Damiano Monticelli*[a], *Sandro Recchia*[a]

[a] *Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, via Valleggio 11, 22100 Como, Italy.*

Analytical methods for trace element speciation have become increasingly important in recent years owing to the growing awareness that the total concentration of elements cannot fully describe their impact on environmental and biological systems. Routine speciation analyses commonly involve the coupling of chromatographic separation techniques (e.g. HPLC) with a sensitive elemental detection system (such as ICP-OES or ICP-MS) ignoring that the high resolving power of HPLC may be redundant when the species to be separated show markedly different chemico-physical properties (i.e. ionic-neutral, cationic-anionic, organic-inorganic). The instrumental apparatus can be greatly simplified under these conditions, as a simple short column with a low number of theoretical plates can be successfully used instead of a HPLC system to separate two (or more) species. As a further simplification, the low backpressure exerted by such short columns allows the direct feeding of the sample solution by a simple peristaltic pump, a standard equipment in ICP-MS and ICP-OES. Such frontal chromatography – ICP-MS (FC-ICP-MS) configuration results in significant cost savings and increased productivity by shortening the analysis time without compromising the high sensitivity typical of ICP-MS, as demonstrated in our recent work on the case of inorganic As(III) and As(V) speciation [1].

In light of the promising analytical performances exhibited by FC-ICP-MS, we decided to extend its applicability to two other speciation issues of environmental interest, i.e. the determination of i) Cr(VI) in natural water and toys [2] and ii) methyl-Hg in biological tissues. Both Cr and Hg speciation involve the presence of a single species (Cr(VI) and Me-Hg) that is largely more relevant under the toxicological point of view compared to the other concurrent species (Cr(III) and inorganic Hg(II), respectively) in the studied matrices. This makes important the selective and highly sensitive detection of such hazardous species. We were able to reach this goal by pushing to the limit the FC approach, i.e. by completely blocking one species, the less relevant one. Regarding Cr(VI) determination, the insertion of a short, homemade column filled with a strong cationic exchange resin in the flow-path of a commercial ICP-MS allows the on-line trapping of cationic Cr(III) and the elution of anionic Cr(VI) when sample solutions acidified with HNO_3 2% are analyzed. As a result, only the Cr(VI) front reaches the detector. An analogous mechanism was exploited for Me-Hg determination in HCl-containing solutions derived from the extraction of MeHg and Hg(II) from biological tissues (e.g. fish muscles): in this case the column is filled with a strong anionic exchange resin to block anionic $HgCl_4^{2-}$ and elute the neutral species MeHgCl. Such separation mechanisms enable the highly selective quantification of Cr(VI) and Me-Hg ultra-traces (LOD = 0.026 µg/kg and 0.010 µg/kg, respectively, in the analyzed solutions) over a wide linearity range (tested up to 1024 µg/kg and 10 µg/kg, respectively) in very short times (60 s and 100 s, respectively). The absence of interferences was verified even in the presence of large amount of the concurrent species, i.e. Cr(III) concentration 50'000-fold higher than Cr(VI) and Hg(II) concentration 100-fold higher than Me-Hg. Key advantages of the proposed FC-ICP-MS methods are the extremely short analysis time, together with the simplicity and cost-effectiveness of FC implementation over a commercial ICP-MS instrumental configuration.

[1] D. Spanu, D. Monticelli, L. Rampazzi, C. Dossi, S. Recchia, *Anal. Chem.* **2019**, *91(21),* 13810
[2] D. Spanu, D. Monticelli, G. Binda, C.Dossi, L. Rampazzi, S. Recchia, *J. Hazard. Mater.* **2021**, *412*, 125280

Identification of protein biomarkers responsible for meat tenderness in bovine *Longissumus* dorsi muscle by Kohonen self-organizing maps and multivariate analysis

Jessica Brandi[a], *Elisa Robotti*[b], *Marcello Manfredi*[c], *Elettra Barberis*[c],
Emilio Marengo[b], *Enrico Novelli*[d], *Daniela Cecconi*[a]

[a]*Department of Biotechnology, University of Verona, Verona, Italy;* [b]*Department of Sciences and Technological Innovation, University of Piemonte Orientale, Alessandria, Italy;* [c]*Department of Translational Medicine and Center for Translational Research on Autoimmune Diseases, University of Piemonte Orientale, Novara, Italy;* [d]*Department of Comparative Biomedicine and Food Science, University of Padua, Legnaro, Padua, Italy.*

Meat tenderness represents one of the most important quality traits required for beef production and consumption. During the last decade proteomic approaches have been applied to identify biomarkers related to the tenderization of bovine meat [1, 2]. The present work aimed at increasing the current panel of biomarkers involved in tenderness of *Longissimus* dorsi (LD) muscle in Charolais cattle.

For this purpose, chemometric approaches have been applied for extracting information from proteomics data. In particular, proteins extracted from Charolais heifer and bull's muscle after 12 or 26 days of aging, were identified by LC-MS/MS and subjected to pattern recognition tools as Principal Component Analysis (PCA) and Kohonen's networks, these last ones, able to identify complex relationships between the variables based on non-linear mapping. Then, Partial Least Squares-Discriminant Analysis (PLS-DA) was applied as classification method, coupled to a variable selection procedure in backward elimination, to identify the biomarkers of tenderization.

These multivariate analyses allowed an exhaustive detection of biomarkers and contemporarily focused on the achievement of models with the highest predictive ability. Indeed, by this approach a total of 58, 43,86 and 97 dysregulated proteins were detected after early, late, long and general ageing, respectively. In particular, down-regulation in hemoglobin subunits and carbonic anhydrase 3 levels was relevant after early ageing, while mimecan and collagen chains levels were reduced after long ageing.

In conclusion, the findings obtained enlarge the panel of biomarkers related to meat tenderness of Charolais cattle, and provides a powerful method based on proteomics and multivariate chemometric techniques that can be applied also in other area of meat science.

[1] Picard, B. and M. Gagaoua, *Food Res Int*, **2020**, *127*, 108739.
[2] M. Gagaoua et al., *Meat Sci*, **2021**, *172*, 108311.

Selection and tuning of bioreagents in SARS CoV-2 serological and antigen rapid testing

Simone Cavalera[a], Fabio Di Nardo[a], Thea Serra[a], Barbara Colitti[b], Emiliana Brocchi[c], Santina Grazioli[c], Cristina Guiotto[d], Franca Fagioli[e], Celeste Cagnazzo[e], Marco Denina[f], Annagloria Palazzo[g], Sergio Rosati[b], Claudio Baggiani[a], Laura Anfossi[a]

[a] Department of Chemistry, University of Turin; [b] Department of Veterinary Sciences, University of Turin, [c]Istituto Zooprofilattico Sperimentale della Lombardia e dell'Emilia-Romagna, [d] A.O. Ordine Mauriziano, Ospedale Umberto I di Torino, [e] Department of Public Health and Paediatrics, Regina Margherita Children's Hospital, University of Turin, [f] Department of Public Health and Paediatrics, Infectious Diseases Unit, Regina Margherita Children's Hospital, Turin, [g] Department of Medical Sciences, Molinette General Hospital, Infectious Diseases Unit

A very well-established technology in the field of rapid diagnosis of infectious diseases is the Lateral Flow ImmunoAssay (LFIA) since it fulfils the requirements for optimal point-of-care testing (POCT) [1]. The LFIAs are based on the antibody/antigen molecular recognition and they provide, most commonly, a visual detection onto test lines drawn with capture bioreagents on a nitrocellulose strip [2]. Such devices are profiled for their diagnostic sensitivity and specificity, that depends on the manufacturer ability and on the quality of the immunoreagents. Concerning the rapid diagnosis of *Severe Acute Respiratory Syndrome Coronavirus-2* (SARS CoV-2), the most common issue in commercial LFIAs has been the low sensitivity, both detecting anti-SARS CoV-2 antibodies (serological test) and detecting viral antigens (antigen test) [3][4]. This was often incorrectly assumed as a limit of the technique. Nevertheless, the presence on the market of some high performance LFIAs for SARS CoV-2 suggests that proper selection and modulation of the involved bioreagents can be the key to reach the challenging sensitivity required to diagnose SARS CoV-2 [5].
Our work focussed on the use of bioreagents in the development of serological and antigen LFIAs for SARS CoV-2 diagnosis. In this study, the bioreagents were functionalised with gold nanoparticles (GNPs) to provide a visual detection and have been explored, selected, and tuned to maximise the sensitivity. In the serological test, non-specific bioreagents such as *Staphylococcal protein A* (SpA) e *Streptococcal protein G* were studied by using the recombinant nucleocapsid protein from SARS CoV-2 (N) for the specific capture of the anti-N antibodies. The tuning of SpA and SpG have been carried by using anti-N antibodies spiked samples, while the diagnostic performances were calculated from testing clinical samples. In addition, samples from cats and dogs were tested exploiting the interspecies versatility of SpA and SpG. Concerning the antigen testing, monoclonal antibodies (mAbs) aiming different N epitopes have been used. The selection, modulation, and eventual combination of the mAbs was made by using recombinant N spiked samples and the diagnostic performances were calculated from SARS CoV-2 positive nasopharyngeal swabs and saliva samples by using two devices. In both the LFIA developments important information is obtained about the role of the bio-ligands and mAbs, and their use alone and combined. The results demonstrated the importance of a proper tuning of the detection bioreagents to achieve high sensitivities [89.9% (CI95 82.7-97.0) for serological SpA-based LFIA, 91,5% (CI95 83,5-99,5) for antigenic on nasopharyngeal swabs and 77,8% (CI95 58.6-97.0) on saliva].

[1] K.J. Land, D.I. Boeras, X.S Ramsay, et al *Nat. Microbiol.* **2019**, *4(1)*, 46-54
[2] M. Saijd, A. Kawde, and M. Daud, *J. Saudi Chem Soc.* **2015**, 19(6), 689-705
[3] M. Döhla, C. Boesecke, B. Schulte, et al *Public Health.* **2020**, 1*82*, 170-172
[4] B. Kabamba-Mukadi, A. Verroken, H. Rodriguez-Villalobos, et al *J. Clin. Virol.* **2020**, *129*
[5] CDC Morbidity and Mortality Weekly Report (MMWR). **2021**, 70(3)

An innovative analytical platform for cannabis chemovar differentiation based on untargeted metabolomics and chemometrics

Andrea Cerrato[a], Sara Elsa Aita[a], Giuseppe Cannazza[b,c] Anna Laura Capriotti[a], Cinzia Citti[b,c], Federico Marini[a], Carmela Maria Montone[a], Aldo Laganà[a,b]

[a] Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy
[b] Department of Life Sciences, University of Modena and Reggio Emilia, Via Giuseppe Campi 287, 41125, Modena, Italy
[c] CNR NANOTEC, Campus Ecotekne, University of Salento, Via Monteroni, 73100 Lecce, Italy

Due to its great genetic plasticity and its ability to grow in different climatic conditions, *Cannabis sativa* has been bred all over the world to create new varieties. C. sativa varieties have been traditionally classified into five chemotypes based on the concentration of the main phytocannabinoids, i.e., tetrahydrocannabinol (THC), cannabidiol (CBD), and cannabigerol (CBG) [1]. However, cannabis chemovars and varieties very often present similar concentrations of such phytocannabinoids but different chemical profiles, which is unavoidably translated into different pharmacological effects when used for therapeutic purposes [2]. For this reason, a more refined approach is needed for chemovar distinction, which was defined phytocannabinomics. The classification was achieved by an analytical platform based on high-resolution mass spectrometry data acquisition, comprehensive characterization of the phytocannabinoid composition thanks to a customized workflow implemented on Compound Discoverer software [3], and validated chemometric data analysis for chemovars differentiation. The method was developed on fifty cannabis varieties, grown under the same conditions, and was validated to discriminate between the standard chemotypes by partial least squares discriminant analysis. Then, the method was extended to consider the entire chemical variety of the cannabis accessions, by an unsupervised approach based on the principal component analysis. The latter approach clearly indicated several new subgroups within the traditional classifications, which arise from a unique composition of the minor phytocannabinoids [4]. The existence of these subgroups, which were never described before, is of critical importance for evaluating the pharmacological effects of cannabis chemovars.

[1] E.P.M. de Meijer; H.J. van der Kamp, F.A. van Eeuwijk, *Euphytica* **1992**, *62*, 187–200.
[2] P. Berman, K. Futoran, G.M. Lewitus, D. Mukha, M. Benami, T. Shlomi, D. Meiri, *Sci. Rep.* **2018**, *8*, 14280
[3] C.M. Montone, A. Cerrato, B. Botta, G. Cannazza, A.L. Capriotti, C. Cavaliere, C. Citti, F. Ghirga, S. Piovesana, A. Laganà, *Talanta* **2020**, *219*, 121310
[4] A. Cerrato, C. Citti, G. Cannazza, A.L. Capriotti, C. Cavaliere, G. Grassi, F. Marini, C.M. Montone, R. Paris, S. Piovesana, *Talanta* **2021**, *230*, 122313

Use of online buffer exchange coupled to native-mass spectrometry to elucidate the stoichiometry of the *Salmonella* FraR (transcriptional repressor)-DNA complex

Angela Di Capua,[a,b] Blake E. Szkoda,[c] Sravya Kovvali,[d] Joy Shaffer,[e] Edward J. Behrman,[a] Venkat Gopalan,[a,c] Vicki H. Wysocki.[a,b,c]

[a]Department of Chemistry & Biochemistry, The Ohio State University, Columbus, OH, USA; [b]Resource for Native MS Guided Structural Biology, Columbus, OH, USA; [c]The Ohio State Biochemistry Program, The Ohio State University, Columbus, OH, USA; [d]Department of Microbiology, The Ohio State University, Columbus, OH, USA; [e]Department of Chemistry and Biochemistry, The University of Texas at Dallas, Richardson, Texas, USA.

Salmonella enterica serovar Typhimurium (*Salmonella*) is a foodborne pathogen that causes gastrointestinal illness and can lead to death. There are no vaccines or antibiotics to specifically combat this bacterium. In 2019, salmonellosis was the second most reported zoonotic disease in the EU, affecting about 88,000 people.[1] During inflammation post-infection, *Salmonella* utilizes fructose-asparagine (F-Asn) as a nutrient. F-Asn is an Amadori product and is converted into glucose-6-phosphate and aspartate through a catabolic pathway that involves different proteins, all encoded by the *fra* operon.[2,3] This work was undertaken to characterize gene regulation of the *fra* operon by FraR, the putative transcriptional factor in this locus.

Native mass spectrometry (MS) is an important analytical tool that is useful for studying protein-protein and protein-ligand (including small molecules and DNA) interactions. The general workflow involves preparing the protein in a volatile buffer (usually ammonium acetate) followed by nano-ESI-MS analysis. However, some proteins can precipitate upon the removal of nonvolatile salts that can stabilize the protein structure.[4] Online buffer exchange (OBE) coupled to native MS is an innovative approach that allows for fast analysis of proteins and protein-ligand complexes.[5] Our OBE approach uses a column packed in-house with P-6 Bio-Gel as the stationary phase and connected to a Vanquish liquid-chromatography system (Thermo Scientific). With OBE, samples can be kept in a non-volatile buffer that favors their native biological properties and then rapidly buffer exchanged into volatile ammonium acetate on-line for mass spectrometric analysis. Here, we used OBE coupled to a Thermo Q Exactive UHMR mass spectrometer to confirm the oligomeric state of FraR and FraR:26-bp DNA complexes, and to investigate 6-P-F-Asp as a potential inducer.

Results from our OBE-native MS studies confirmed the dimeric state of FraR, consistent with dimers shown previously for other members of the GntR family,[5] and showed that a FraR dimer binds the 26-bp DNA. In addition, we show that 6-P-F-Asp can bind to FraR and trigger FraR dissociation from the DNA. These findings provide a first glimpse into the regulation of Amadori metabolism in a clinically significant bacterial pathogen.

[1] https://www.ecdc.europa.eu
[1] Ali, M. M. *et al*. *PLoS Pathogen*, **2014**, *10 (6)*, e1004209.
[2] Sabag-Daigle, A. *et al. Scientific Reports* **2016**, *6*, 28117.
[3] Xia, Z. *et al. Analyst* **2019**, *144*, 2565–2573.
[4] VanAernum, Z.L., Busch, F., Jones, B.J. *et al. Nat Protoc*, **2020**, *15*, 1132–1157.
[5] Graf von Armansperg B, Koller F, Gericke N, *et al. Mol Microbiol*., **2021**, *115(2)*,175-190.

Exploiting silver nanoplates as colorimetric label in Lateral Flow Immunoassay

Fabio Di Nardo[a], Marco Zannotti[b], Simone Cavalera[a], Matteo Chiarello[a], Andrea Rossi[b], Rita Giovannetti[b], Laura Anfossi[a], Claudio Baggiani[a]

[a] *Chemistry Department, University of Torino, 10125 Turin, Italy;* [b] *School of Science and Technology, Chemistry division, University of Camerino, 62032 Camerino, Italy*

The Lateral Flow Immunoassay (LFIA) is one of the most successful paper-based (bio)analytical technique for the on-site detection of target substances, where the sample is added on a standalone device and the result is obtained in a few minutes. This analytical platform has been commonly known for the pregnancy tests and now is taking the footlights for the COVID-19 rapid tests.

Typically, colorimetric LFIAs employ spherical gold nanoparticles (s-GNPs) as labels [1]. This choice is mainly due to their simple preparation, strong surface plasmon resonance (SPR) in the visible spectroscopy region (around 520 nanometers), high extinction coefficients, and easy conjugation to antibodies (Ab) that are the most extensively used recognition elements in LFIA [2]. As a consequence, the use of s-GNPs allows to evaluate the assay results just by the naked eye without the use of additional instrumentation.

Besides common s-GNPs, during the last decades, the use of other colorimetric labels have been exploited to try to improve the analytical performances of the assay and its versatility. The use of other noble metal nanoparticles that shares some of the desirable peculiarities of s-GNPs can be considered a choice worthy of further study.

In this work, different silver nanoplates (AgNPs), previously applied to develop a plasmon sensor for the detection of Hg^{2+} [3], have been evaluated as an alternative label in LFIA.

In order to assess their suitable use, a preliminary study on the passive adsorption of antibodies on the AgNPs as a function of the medium and the amount of Ab used for conjugation with AgNPs was conducted. Both the stability of the sol and the performance of the labeled antibodies in model LFIAs, in terms of signal intensities and analytical sensitivity, were considered.

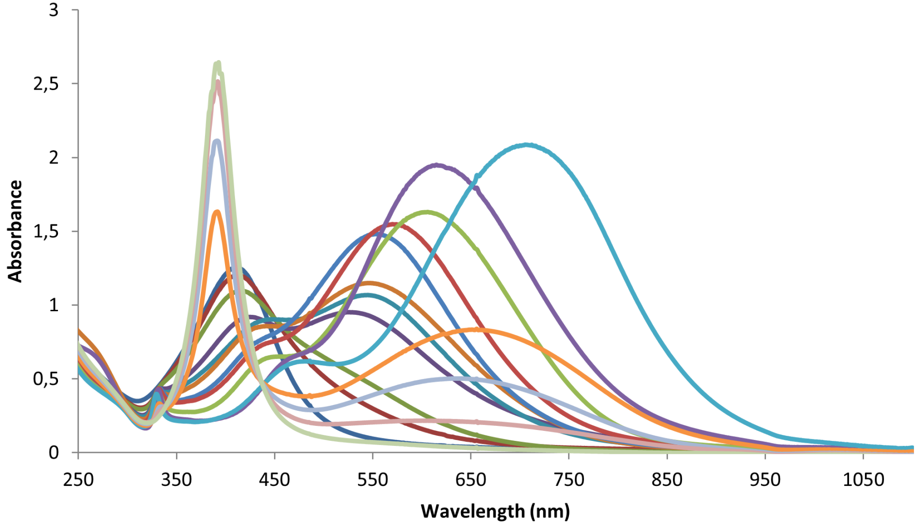


Figure 1. UV-Vis spectra of the different AgNPs evaluated in the study.

[1] F. Di Nardo, C. Baggiani, C. Giovannoli, G. Spano, L. Anfossi, *Microchim. Acta* **2017**, *184*, 1295.

[2] B. O'Farrell, *Topics Compan. Anim. Med.* **2015**, *30*, 139.

[3] M. Zannotti, V. Vicomandi, A. Rossi, M. Minicucci, S. Ferraro, L. Petetta, R. Giovannetti, *J. Mol. Liq.* **2020**, *309*, 113238.

UPLC-Q-TOF-MS/MS analysis of bile acids and their main metabolite profile in farm animal faeces and species-specific correlation with gut microbiota

Emanuele Porru[a], Daniel Scichitano[b], Nicolò Interino[a], Marco Candela[b], Aldo Roda[a,c], Jessica Fiori[a,d]

[a] Department of Chemistry "Giacomo Ciamician", University of Bologna; [b] Department of Pharmacy and Biotechnology, University of Bologna; [c]INBB-Biostructures and Biosystems National Institute,Rome; [d]Interdepartmental Center for Industrial Research–CIRI-MAM, University of Bologna, Bologna, Italy

There is a growing interest in the named "acidic sterolbioma", that is the genetic potential of the gut microbiome to produce and transform bile acids (BAs). Faecal BA composition is strictly related to gut microbiota (GM) which is responsible for the production of BA metabolites including dehydroxylated secondary BAs and oxo-BAs. In this context, the quali-quantitative complete BA profile, as microbiome-host co-metabolic products, is fundamental to study the GM-host interaction in mammalians both in physiological and pathological conditions [1]. As a contribute to shed light on this correlation, we investigated the acidic sterolbioma products in several animals, mainly livestock, as a powerful species-specific biomarker correlated to GM and host diseases.

To this end, we developed and validated a comprehensive and fast reversed phase ultra-performance liquid chromatography - quadrupole time-of-flight tandem mass spectrometry (RP-UPLC-Q-TOF-MS/MS) method for the analysis of up to 30 BAs in faeces of 10 vertebrate species, including 21 oxo-BAs (which represent in human approximately 20-30% of the total faecal Bas [2]) and their metabolic precursors. Gradient elution chromatographic separation was obtained in 10 minutes with high analytical performance in terms of selectivity, sensitivity (LOQ from 0,05 to 0.1 ug/ml), accuracy (bias% $\leq$ 5%), precision (CV% $\leq$ 5%) and matrix effect (ME% $\leq$ 10%). The fast solvent extraction method was evaluated for all BAs in each animal with high recovery percentage (Rec% > 95). The wide range of response linearity (over three order of magnitude, from 0.05 to 100 ug/ml) and the use of isotopically labelled internal standards allowed to quantify the BAs and their GM metabolites in several animal species.

Parallel, the gut microbiota assessment in farm animals was evaluated through 16S rRNA next generation sequencing, and the correlation was performed by multivariate analysis, allowing to reconstruct species-specific associations between the BAs profile and specific GM components.

[1] Ridlon, J. M.; Bajaj, J. S. *Acta Pharm. Sin. B* **2015**, *5* (2), 99–105.

[2] Franco, P.; Porru, E.; Fiori, J.; Gioiello, A.; Cerra, B.; Roda, G.; Caliceti, C.; Simoni, P.; Roda, A. *J. Chromatogr. A* **2019**, *1585*, 70–81.

Nanosphere, polymer, self-assembled material? Clearing up the confusion on polydopamine through multidetection-FFF

V.Marassi [a b], *A. Mavridi- Printezi* [a], *S. Giordani* [a], *B. Roda* [a b], *A.Zattoni* [a b], *M. Montalti* [a], *P.Reschiglian* [a b]

[a] *Dept. of Chemistry G Ciamician, University of Bologna, Italy;* [b] *byFlow srl, Bologna, Italy*

Melanin-based nanoparticles excel for their extraordinary combination of optical, electronic, chemical, photophysical, and photochemical properties. Melanin synthetic analogue, polydopamine (PDA), displays the same optical, electronic and magnetic properties to the natural pigment, possessing also excellent biocompatibility. Additionally, PDA owns many functional groups, such as catechol, amine, and imine, that can either covalently bind or non-covalently load different active agents. With these benefits, PDA can be used for a wide range of application acting as coating material, as carrier or as the active component for bio-application. Though it is believed that the involved stages could resemble the natural melanin synthetic pathway, the polymerization mechanism of PDA remains unclear and its molecular structure is still under discussion, hindering application to the full potential of this material. Some studies claim PDA consists of monomers crosslinked by strong non-covalent bonding. Others suggested that PDA is made of supramolecular structures of unpolymerized dopamine self-assembled with oxidative polymerization products; some propose covalent, polymeric structures; the presence of a mixture of these species is also hypothesized [1,2].
In our approach, we exploited multidetection-FFF to investigate the structural complexity of freshly synthesized PDA. The benefits include high recovery and short analysis time, the ability to work in the synthesis environment and at the native state, multidimensional characterization of the detected species (by means of spectroscopy and laser scattering), and the collection of purified fractions [3].
An optimized separation method showed that PDA is present as two differently eluted species. Though they share the same UV absorption spectrum, a different emission is observed demonstrating a different arrangement effecting π-π stacking and interactions. The first species was predominant in relative abundance, was arranged as a coiled structure, and had lower molar mass and hydrodynamic radius (<25nm) when compared to size standards in the same conditions. The second corresponded to monodispersed, solid spheres with a radius of about 85 nm, while its molar mass was two orders of magnitude greater. Centrifugation of the sample could enrich the two populations in the supernatant and pellet, but at the cost of monodispersity. The two species were attributed to 1. A conventional, covalent polymer lacking structural organization and 2. A stable supramolecular system with a defined radius. Dilution, heat treatment and microwave radiation did not modify the species ratio, proving that the two systems coexist and are formed independently in the synthesis process. These new insights are not only the first observation of the simultaneous dual nature of PDA, but can also help justify contradicting literature. Moreover, FFF separation provided practical improvements towards the purification and subsequent use of high-quality, monodispersed PDA nanospheres, overcoming the limitations of centrifugation.

[1] D.R. Dreyer, D.J. Miller, B.D. Freeman, D.R. Paul, C. Bielawski, *Langmuir* **2012**, *28*, 6428–6435.
[2] Mavridi-Printezi A., Guernelli M., Menichetti A., Montalti M, *Nanomaterials* **2020**, *10*, 2276
[3] V. Marassi, D. Calabria, I. Trozzi, A. Zattoni, P. Reschiglian, B. Roda, *J Chrom A*, **2021**, *1636*, 461739

Insights into aptamer-protein interactions for analytical applications: egg white lysozyme as case study

Monica Mattarozzi[a], *Lorenzo Toma*[a], *Marco Giannetto*[a], *Luca Ronda*[b], *Valentina Marassi*[c], *Pierluigi Reschiglian*[c], *Maria Careri*[a]

[a] *Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Italy;* [b] *Department of Medicine and Surgery, University of Parma, Italy;* [c] *Department of Chemistry, University of Bologna, Italy*

Aptamers are short DNA or RNA single-stranded oligonucleotides selected *in vitro* for their ability to bind a wide variety of target compounds with high affinity and specificity. Significant advantages over antibodies, such as easy and reproducible synthesis, convenient chemical modification and high stability have led to growing analytical interest in aptamers as emerging recognition elements. In many cases aptamer binding assays are not robust and straightforward: actually, there is an urgent need to go beyond the proof of concept [1], taking into account the challenges for the practical and reliable application of aptamer-based strategies when facing analytical problems [2]. In addition, aptamer-based strategies can be prone to artifacts and data misinterpretation due to the lack of rigorous multifaceted characterization of aptamer-target interaction [3].

In this context, the aim of the present research project was the development of innovative and reliable analytical strategies based on aptamers for the determination of egg white lysozyme in food as protein of food allergy concern. The activities focused on the development of (i) a competitive electrochemical magnetic apta-assay and (ii) aptamer-based magnetic solid phase extraction method followed by LC-MS/MS analysis. Attention was primarily paid to compare for the first time the binding efficiency of different DNA aptamer sequences for egg white lysozyme, including also randomized and unrelated sequences as negative controls.

The 5'-aminolink modified aptamers were immobilized on carboxylate magnetic microbeads and different aptamer concentrations were investigated for the functionalization step.

It is well known that experimental conditions such as composition, pH and ionic strength of the binding medium strongly affect the structures of the aptamers as well as the binding process [4]. On this basis, we devised a very simple electrochemical apta-assay involving biotin-labelled lysozyme as model in order to directly assess aptamer-target binding. Different blocking strategies were investigated to reduce non-specific interactions. The effect of the binding buffer was also studied. The devised electrochemical apta-assay and circular dichroism analysis proved effective as a multi-technique platform to give insights into binding performance of aptamers with their protein target. The feasibility of fluorescence energy transfer technique and field-flow fractionation will be investigated towards a further in depth-study of aptamer-target binding. This study represents a promising starting point for the development and design of reliable aptamer-based analytical strategies and will facilitate researchers to address many of the concerns faced by current aptamer development.

[1] Y. Wu, I. Belmonte, K. S. Sykes, Y. Xiao, R. J. White RJ, *Anal. Chem.* **2019**, *91*,15335.

[2] M. Mattarozzi, L. Toma, A. Bertucci, M. Giannetto, M. Careri, *Anal. Bioanal. Chem.*, *submitted*.

[3] F. Bottari, E. Daems, A.-M. de Vries, P. Van Wielendaele, S. Trashin, R. Blust, F. Sobott, A. Madder, J. C. Martins, K. De Wael, *JACS* **2020**, *142*, 19622.

[4] T. Hianik, V. Ostatná, M. Sonlajtnerova, I. Grman, *Bioelectrochemistry* **2007**, *70*, 127.

Untargeted metabolomics reveals different postprandial serum metabolome profiles after single intake of *Vaccinium myrtillus* and *Vaccinium corymbosum*.

Lapo Renai [a], *Marynka Ulaszewska* [b], *Claudia Ancillotti* [a], *Mar Garcia-Aloy* [c], *Fulvio Mattivi* [c], *Massimo Del Bubba*[a].

[a] *Department of Chemistry, University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italy.*
[b] *IRCCS San Raffaele Scientific Institute, Center for Omics Sciences, Proteomics and Metabolomics Facility - ProMeFa, Milan, Italy.*
[c] *Department of Food Quality and Nutrition, Fondazione Edmund Mach, Research and Innovation Centre, San Michele all'Adige, Italy*

Berries consumption is increasingly associated to the prevention of several chronic diseases and neoplasm formation due to their high content of antioxidant compounds, such as (poly)phenolic compounds, reducing the oxidative stress related to these pathologies [1]. The berries belonging to the *Vaccinium* genus, above all *V. myrtillus* berries (i.e., bilberry), have been suggested as functional foods and largely used for supplement preparation [2]. Bilberry extracts already showed anti-proliferative and apoptotic effects in *in vitro* studies on model cancer cell lines [3].

However, there is still a strong knowledge gap in (i) the identification of the gut metabolites originated by berries intake and how they behave to exert their chemopreventive action, and in (ii) the side antioxidant capacity of other berry constituents.

Accordingly, the aim of this research is the application of an untargeted liquid chromatography-high resolution tandem mass spectrometry (LC-HRMS) platform on the analysis of serum significant metabolites in healthy volunteers after the administration of *V. myrtillus* (VM) and *V. corymbosum* (VC) berry supplements, being the widest consumed *Vaccinium* species.

Under these experimental conditions, the selection of statistically significant features and their in-depth annotation process performed by advanced bioinformatics tools allowed to identify twelve relevant serum metabolites suitable to the discrimination of VM and VC intakes, belonging to the categories of purine pathway metabolites, benzoic and benzodiol metabolites, indole alkaloids, abscisic acid derivatives, organic acids, and fatty acids. Hydroxy-hippuric acid and azelaic acid were annotated at level I, whereas the annotation of majority of the remaining metabolites was deepened up to level II.

In addition, this study permitted to significantly distinguish metabolome profiles between two berries supplementation, discriminated by abscisic acid glucuronide, citric acid, hydroxy hippuric acid and methyl-catechol sulphate.

[1] M. Ulaszewska, M. Garcia-Aloy, *Genes & Nutrition.* **2020**, *15*, 17.
[2] C. Ancillotti, L. Ciofi, *Anal Bioanal Chem.* **2017**, *409*, 1347-1368.
[3] M. Del Bubba, C. Di Serio, *Phytotherapy Research.* **2021**, *35*, 1089-1098.

Analytical methods in clinical lipidomics: HPLC and SFC comparison for the analysis of lipid mediators in clinical samples

Adriana Arigò[a], *Francesca Rigano*[a], *Paola Dugo*[a,b,c,d], *Luigi Mondello*[a,b,c,d]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[c] *Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy;*
[d] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

Clinical lipidomics refers to the detailed determination of lipids in medical diagnostic samples. The presence of specific metabolites in biological fluids, or their content over limit levels, is representative of pathologic conditions [1, 2]. Lipid mediators, also known as eicosanoids, are mainly derivatives by enzymatic or non-enzymatic oxidation of arachidonic acid and other polyunsaturated fatty acids (PUFAs). These compounds were selected as biomarkers for several pathologies, consequently their assessment in biological fluids, such as blood, serum, plasma, urine, *etc.* is a powerful approach for clinical purposes. Highly sensitive methods are required to investigate lipid mediators, due to their low concentration in the matrix.

In this study, several parameters related to the separation and the tandem mass spectrometric detection were evaluated for liquid (LC) and supercritical fluid chromatography (SFC) applied to target eicosaonoids. A column screening was carried out to select the best stationary phase for each technique and mass spectrometric parameters were tested to achieve the best conditions in terms of intensity of the signal and data points.

The Multiple Reactions Monitoring (MRM) spectrum concept, based on the optimization of several transitions for each target, was applied and a LC multi MRM spectra library was created.

The research focused on 42 selected compounds, among arachidonic, eicosapentaenoic and docosahexaenoic acids derivatives. Lipid mediators with different clinical meanings were selected according to the finding that the abundance of independently lipid molecules would better reflect pathogenic process instead of single lipid species [2].

The limits of the SFC technique, corroborated by previous research [3], are discussed whereas the analysis of real samples show the potential of the developed methods in medical applications.

[1] C.C. Theo, *et al.*, *TrAC.* **2015**, *66*, 1.
[2] O. Vvedenskaya, *et al. TrAC.***2019**, *120*, 115277.
[3] R. Berkecz, *at al.* J Chrom A. **2017**, *1511*, 107.

LC-MS/MS data integration of quantitative proteomics and lipidomics to study the effects of bioactive compounds

Radrezza S.[a]*, Aiello G.*[a]*, Fedorova M.*[b]*, Depta G.*[c]*, Aldini G.*[a]*, Carini M.*[a]*, D'Amato A.*[a]

[a]*Department of Pharmaceutical Sciences, University of Milan, Via L. Mangiagalli 25, 20133 Milan, Italy*
[b]*Institute of Bioanalytical Chemistry, Faculty of Chemistry and Mineralogy, University of Leipzig, Deutscher Platz 5, 04103 Leipzig, Germany*
[c]*Intercos S.p.A., Via Marconi 84, 20864, Agrate Brianza, MB, Italy*

The development of highly reproducible nano HPLC separation, high resolution mass spectrometers, and bioinformatics tools greatly improved the reliability and accuracy of nLCMS/MS analysis of proteins and lipids and their integration to study biological systems. In the present study we focus on the application of an integrated approach to understand the effect of low molecular weight Hyaluronic Acid (LMW-HA) in human dermal fibroblasts. Our previous study, adopting nLC-MS/MS (Orbitrap Fusion™ Tribrid™ coupled with UltiMate™ 3000 RSLCnano System), for label free quantitative proteomics, showed regulation of intra- and extra-cellular pathways such as extracellular matrix reorganization, proteoglycans and collagen biosynthesis. Moreover, cell's wellness was confirmed despite the inflammation and immune response [1]. This approach resulted in a huge amount of data correlating with variation of lipidome, regulator of important cellular processes too [2,3]. Untargeted lipidomics based on μLC- MS/MS (Q ExactivePlus Hybrid Quadrupole-Orbitrap coupled with Vanquish Horizon system) analyses allowed us to detect a total of 1380 lipids (n= 923 in positive mode; n= 457 in negative mode) unique by structure. Triacylglycerols, ceramides and phosphatidylcholines were the most represented classes. The protein quantitative data were integrated with lipid expression by the IPA software. More than 20 functional modules including 26 lipids belonging to different classes and several differentially regulated proteins were found covering several intra- and extra-cellular functions including lipid, vitamin and mineral metabolism, cell signaling and molecular transport. In conclusion, the integration of data obtained by LC-MS/MS based on quantitative proteomics and lipidomics is a powerful approach in bioanalytical chemistry. This can be used to describe biological network changes in cell or animal models upon treatment with bioactive compounds.

[1] Radrezza S., Baron G., *JPBA*, **2020**,185, 113199.
[2] Joyce A.R., Palsson B. *Molecular Cell Biology. Nature*, **2006**. DOI: 10.1038/nrm1857
[3] Wenk, M. R. *Cell*, **2010**, 143, 888–895.

Multicolumn Countercurrent Solvent Gradient Purification (MCSGP) process for the intensification of the polishing step of a bioactive peptide mixture

C. De Luca[a], S. Felletti[a], D. Bozza[a], G. Lievore[a], A. Buratti[a], M. Morbidelli[b], M. Macis[c], A. Ricci[c], W. Cabri[c,d], A. Cavazzini[a], M. Catani[a]

[a] Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, 44121 Ferrara, Italy; [b] Department of Chemistry, Materials and Chemical Engineering Giulio Natta, Politecnico di Milano, via Mancinelli 7, 20131 Milan, Italy; [c] Fresenius Kabi iPSUM srl, I&D, Via San Leonardo 23, 45010 Villadose (Rovigo), Italy; [d] Department of Chemistry Giacomo Ciamician, Alma Mater Studiorum-University of Bologna, Via Selmi 2, 40126 Bologna, Italy

Pharmaceutical products, including peptides, must satisfy very strict purity specifications, because of quality and safety reasons. Therefore, the necessity to operate one or more purification steps to obtain high quality drugs is indisputable. Critical impurities chemically very similar to the target product are generated during the synthesis and are generally removed by means of preparative single-column chromatographic techniques (=batch methods) [1,2]. Batch methods struggle to separate completely the peptide of interest from other groups of impurities, because of their similarity and of high loading of sample processed in preparative conditions, which cause peaks overlapping [3]. The typical situation encountered in these cases is the so-called center-cut separation, where the target elutes as intermediate between two other groups of impurities less and more retained respectively. The direct consequence of this apparently insurmountable overlapping is a yield-purity trade-off, a limit intrinsic to batch chromatography according to which it is possible to obtain either high purity or high recovery of the peptide of interest, depending on whether the overlapping windows are collected or not [4]. This trade-off leads to drawbacks in the overall economy of the process. Multicolumn chromatographic processes, operating in continuous and countercurrent mode, can alleviate this limitation by performing internal recycling of the overlapping portions of the chromatogram [5]. The technique used in the frame of this research is twin-column Multicolumn Countercurrent Solvent Gradient Purification (MCSGP), which has been applied to the purification of an industrial crude of a bioactive decapeptide. It has been demonstrated that MCSGP leads to promising results, including a remarkable improvement in process performance (up to 6 times higher) from the point of view of recovery, productivity and solvent consumption, with respect to the corresponding batch run. The automation of the process on industrial scale would lead to great reproducibility which would reflect in improved consistency in product quality.

[1] C. De Luca; S. Felletti; G. Lievore; A. Buratti; S. Vogg; M. Morbidelli; A. Cavazzini; M. Catani; M. Macis; A. Ricci; W. Cabri, *J Chromatogr A* **2020**, *1625*, 1-7.
[2] C. De Luca; S. Felletti; G. Lievore; T. Chenet; M. Morbidelli; M. Sponchioni; A. Cavazzini; M. Catani, *Trends Analyt Chem* **2020**, *132*, 1-8.
[3] S. Vogg; N. Ulmer; J. Souquet; H. Broly; M. Morbidelli, *Biotechnol J* **2019**, *1800732*, 1-8.
[4] T. Müller-Späth; G. Ströhlein; O. Lyngberg; D. Maclean, *Chem Today* **2013**, *31*, 56-60.
[5] F. Steinebach; T. Müller-Späth; M. Morbidelli, *Biotechnol J* **2016**, *11*, 1126-1141.

Enzyme inhibition coupled to Molecular Imprinted Polymers for acetazolamide determination in biological samples

Dounia Elfadil[1,2], *Sara Palmieri*[1], *Flavio Della Pelle*[1], *Manuel Sergi*[1], *Aziz Amine*[2], ***, *Dario Compagnone*[1] ***

[1]*Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, via Renato Balzarini 1, 64100 Teramo, Italy*
[2]*Laboratory of Process Engineering and Environment, Faculty of Sciences and Techniques, Hassan II University of Casablanca, Mohammedia, Morocco*

Several methods involving MIPs devoted to extract and analyze sulphonamide from different matrices are reported [1, 2], however, the unresolved analytical issue relise in obtaining intra-class selectivity between sulfonamides. Here is presented for the first time a method coupling molecularly imprinted polymers (MIPs) and enzymatic inhibition assay, for the sensitive and selective determination of acetazolamide (ACZ) in biological samples.
To reduce the number of trials and achieve high selectivity, molecular modeling was employed before MIPs synthesis. Then, the MIPs were synthesized by thermal initiated polymerization in acetone, using acrylamide as functional monomer and ethylene glycol dimethacrylate as cross-linker, logically, ACZ was used as a template molecule.
The MIPs were used as a sorbent phase in dispersion solid-phase extraction (MIPs-dSPE) and the optimal working parameters selected, LC-MS analysis confirmed the MIPs ability to retain ACZ in model solutions. Finally, to obtain a selective and sensitive method, the MIPs-dSPE was combined with an enzymatic inhibition colorimetric assay based on the carbonic anhydrase, an enzyme inhibited by specific sulfonamides. Afterward, the developed MIPs/enzymatic-based method was applied for the determination of ACZ in biological samples.
The developed combined method allowed to reliably determine ACZ and Diamox (a drug containing ACZ) in serum and human blood, with outstanding recoveries (95-97%). Noteworthily, others sulfonamides and sulfonamides containing drugs, not affected the ACZ analysis.

In the here proposed strategy, the double selectivity (MIPs + enzyme) and the enzyme-improved sensitivity, allowed to obtain a method able to quantitatively determine ACZ and ACZ-containing drugs in biological samples.

[1] Shi Xizhi, Yuan Meng, Jinghua Liu, Aili Sun, Dexiang Li, Chunxia Yao, Yin Lu, Jiong Chen, *J. Chromatogr. B.*, **2011**, 879, 1071-76.

[2] Zhao Xiaolei, Junying Wang, Junping Wang, Shuo Wang, *J. Chromatograp. A*, **2018**, 1574, 9-17.

Determination of salivary short chain fatty acids and hydroxy acids in heart failure patients by in-situ derivatization and Hisorb-probe sorptive extraction coupled to thermal desorption and gas chromatography-tandem mass spectrometry

Alessio Lenzi[a], *Denise Biagini*[a], *Silvia Ghimenti*[a], *Federico Vivaldi*[a], *Andrea Bonini*[a], *Pietro Salvo*[b], *Roger Fuoco*[a], *Fabio Di Francesco*[a] *and Tommaso Lomonaco*[a]

[a] *Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, Pisa, Italy.*
[b] *Institute of Clinical Physiology, CNR, Via G. Moruzzi 3, Pisa, Italy.*

Short chain fatty acids (SCFAs) are the predominant products of dietary fiber fermentation operated by gut microbiota. Their variation in human can emphasize the predisposition to metabolic diseases. Studies have also highlighted their implication in the regulation of blood pressure, and in the increased risk of Heart Failure (HF) [1]. On the other hand, compounds unrelated to microbiota activity, such as 3-hydroxybutyric acid and lactic acid, are used as energy sources during acute energies crisis. In the last few years, a link between oral and gut microbiomes was underlined. Differences in the oral metabolome, as for example in the SCFAs family of compounds, are known to be correlated to the health of salivary microbiome, which is also related to the development of a low-grade inflammation in the host, and consequently to potential increasing risks of cardiovascular diseases [2].

The aim of this work was to develop and validate an analytical procedure based on an innovative single step in-situ derivatization with pentafluorobenzyl bromide (PFB-Br) and HiSorb-probe sorptive extraction for the determination of a panel of low-molecular weight salivary metabolites (SCFAs, 3-hydroxybutyric acid, and lactic acid). Reaction's derivatives released from HiSorb probe by thermal desorption were analyzed by gas chromatography-tandem mass spectrometry. A Central Composite Face-Centered experimental design was used for the optimization of the molar ratio between PFB-Br and target analytes, the derivatization temperature and time which resulted respectively 100, 60 °C and 180 min. A sample volume of 20 µL of saliva guaranteed limits of detection between 0.1-100 µM. Intra- and inter-day precision and recovery were in the range of 10-15% and 70-98%, respectively, thus highlighting the reliability of the method.

The validated method was employed as a proof-of-concept approach to monitor and compare SCFAs and hydroxy acids collected from saliva of HF patients during hospitalization. Likewise, the method was employed to follow-up patients suffering from chronic heart failure, hypertension, and obesity in order to preliminary evaluate the role of these compounds as potential salivary markers of disease progression.

[1] L.B. Richards, M. Li, B.C.A.M. van Esch, J. Garssen, G. Folkerts, *PharmaNutrition*, **2016**, 4, 68-111

[2] M. Pietiäinen, J.M. Liljestrand, E. Kopra, P.J. Pussinen, *Eur. J. Oral Sci.*, **2018**, 126, 26-36

Metaproteomics and metabolomics investigation of microbiome alterations in pediatric obese subjects

Elettra Barberis[a,b], Chiara Merlo[c], Virginia Vanella[a,b], Emilio Marengo[d], Roberta Ricotti[e], Flavia Prodam[e], Marcello Manfredi[a,b]

[a] *Department of Translational Medicine, University of Piemonte Orientale, Novara, Italy;* [b] *Center for Translational Research on Autoimmune and Allergic Diseases, University of Piemonte Orientale, Novara, Italy;* [c] *ISALIT, Novara, Italy;* [d] *Department of Sciences and Technological Innovation, University of Piemonte Orientale, Novara, Italy;* [e] *Department of Health Sciences, University of Piemonte Orientale, Novara, Italy.*

Although the study of intestinal microbiome is still challenging, today, thanks to recent developments of metaproteomics and metabolomics, the gut microbiome characterization is possible. In fact, metaproteomics involves non-targeted shotgun mass spectrometry to assess the diversity and abundance of microbial proteins, while metabolomics can be used to study the impact gut microbiome on small molecules production.

In the present research we combined untargeted metaproteomics and metabolomics to study alterations of the gut microbiome in pediatric obese patients subjected to a dietary intervention with Mediterranean diet. Microbiome was characterized before and after six and twelve months of intervention. Metaproteomics analysis was performed using a nano-LC chromatography coupled to high-resolution mass spectrometer (Triple TOF 5600+, Sciex), while metabolomics analysis was carried out using a bi-dimensional gas chromatography coupled to mass spectrometry (GCxGC-TOFMS, Pegasus BT 4D, LECO). Short chain fatty acids (SCFAs) analysis was also performed on serum using GC-MS.

The metaproteomic approach allowed the identification of more than 100000 peptides and more 35000 proteins. Phylogenetic and functional changes of the bacterial composition were observed in relation to the dietary intervention and BMI reduction. Changes associated with the improvement of the intestinal inflammatory state and functional alterations directly dependent on the diet were also detected. The metabolomics analysis revealed a decrease of the fecal acetic acid, propionic acid and butyric acid after twelve months of treatment. Acetic acid and butyric acid decreased also in serum. High levels of SCFAs were already found in obese patients.

Our results showed that Mediterranean diet induced in pediatric obese patients an increasing of the Bacteroidetes/Firmicutes ratio, which brought to a lower production of SCFAs in the intestine and thus a reduction of circulating SCFAs. In addition a global reduction of microbial species associated to inflammatory state were identified.

In conclusion, mass spectrometry can play a central role in the study of the interaction of the gut microbiome with the human health state.

A simple and Fast Multiresidue Method for determination of hormones in vegetables and fruits

Francesca Merlo[a], *Sara Suppini*[a], *Federica Maraschi*[a], *Antonella Profumo*[a], *Andrea Speltini*[a,b].

[a]*Department of Chemistry, University of Pavia, 27100 Pavia, Italy;*
[b]*Department of Drug Sciences, University of Pavia, 27100 Pavia, Italy.*

This study is focused on the development of a multiresidue analytical method for determination of steroid hormones (progestins, oestrogens, androgens and glucocorticoids) in vegetables and fruits. Pollutants' presence -especially those with endocrine disrupting properties as steroid hormones- in edible plants is a topic of high concern, related to the use of reclaimed wastewaters for irrigation. Once in the soil, plant uptake, root accumulation or translocation to the leaves and fruits can occur depending on the physicochemical properties of the contaminants (pK_a and $\log K_{ow}$). The herein considered analytes present a wide $\log K_{ow}$ range, from 1.46 of Cortisone to 4.02 of 17β-estradiol, thus they tend to accumulate differently in edible parts (e.g. roots, leaves and fruits). Therefore, a root vegetable (carrot), a leafy vegetable (spinach), and a fruit (strawberry) were chosen as probes for this study.

Ultrasound-assisted extraction (UAE) has been selected due to its short extraction times, reduced organic solvent consumption, energy and costs saved. The extraction procedure was studied in freeze-dried matrices, processing samples before (blank matrices) and after spiking (for each analyte 100 ng g^{-1} dry weight). Firstly, the role of different extraction solvents, namely Acetone (ACE), Methanol (MeOH), Acetonitrile (ACN), mixture MeOH: ACN (75:25, v/v) and mixture MeOH: ACN (50:50, v/v), was evaluated. A single extraction was performed (5 mL of solvent, 5 min, r.t.). The extract was evaporated to dryness under N_2 stream, reconstituted in 1 mL of MeOH, and analysed by HPLC–MS/MS. The best overall performances in terms of recovery (%R) and matrix effect (%ME) were achieved with MeOH (%R in the range 50-84%, ME in the range 14-45%, depending on analyte and matrix, *n=3*) as demonstrated by ANOVA test. The extraction efficiency was then optimized by a chemometric approach to develop a multiresidue method. A 2^3 factorial design was constructed considering three variables at two levels: number of cycles (1 and 3); solvent volume (2 and 5 mL); sonication time (1 and 10 min). Each one of the eight experiments was replicated three times, once for each matrix. The multi-analyte recovery was selected as the experimental response for each experiment. The elaboration (R-based software CAT, Chemometric Agile Tool) showed that the number of cycles is significant with $p < 0.01$ (**) like the interaction between number of cycles and solvent volume. Accordingly, the optimized extraction is comprised of 3 x 1 min ultrasonic cycles with a small volume of organic solvent (2 mL MeOH). To reduce matrix effects resulting from co-eluting residual matrix components, an additional clean-up step was studied entailing different sorbent materials and approaches: Activated Chemviron Carbon (d-SPE), Florisil (SPE), Primary-Secondary Amine (SPE), C18 (SPE), SUPERCLEAN^{TM} LC-NH_2 (SPE). The latter was selected as SPE sorbent for the clean-up because it is able to retain most of matrix co-extracted interferences. The final analytical method was successfully applied for multiresidue extraction at lower concentrations (for each analyte 10 and 50 ng g^{-1} dry weight) with good recoveries (%R in the range 65-121% for carrot, 89-130% for spinach, 66-105% for strawberry) and repeatability (RSD < 10% for all the matrices). These appealing results together with relative low detection limits suggest the suitability of the method to monitor the presence of these emerging contaminants in vegetables and fruits and their potential uptake.

[1] E. L. Miller, S. L. Nason, K. G. Karthikeyan, J. A. Pedersen, *Environ. Sci. Technol.* **2016,** 50, 525–541.
[2] X. Wu, L. K. Dodgen, J. L. Conkle, J. Gan, *Sci. Total Environ.* **2015**, 536, 655–666 .
[3] K. M. Bagheri, D. Al-jabery, J. G. B. Wunsch, *Sci. Total Environ*. **2020**, 698, 133999.

Microwave distillation technique for the isolation of *Cannabis Sativa L.* essential oils and GC-MS/FID analysis for terpenes and terpenoids characterization.

Giuseppe Micalizzi[a], Filippo Alibrando[a], Federica Vento[a], Paola Dugo[a,b,c] and Luigi Mondello[a,b,c,d]

[a] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*
[b] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*
[c] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*
[d] *Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy*

Cannabis essential oil is attracting more and more attention from different industries due to the typical and unique smell of this plant. Therefore, the enormous interest of the global flavor and fragrance market led the authors to develop a solventless microwave assisted hydro-distillation (MAHD) technique for the distillation and isolation of hemp essential oil from fresh and dried inflorescences. In addition, a detailed study of the volatile fraction including terpene, terpenoid and cannabinoid compounds was performed by gas chromatographic analysis. In such respect, the monitoring of these compounds is fundamental considering their probable contribution to the pharmaceutical properties of cannabis-based medical products [1]. In order to establish the authenticity of natural cannabis essential oils, an enantio-GC-MS method was also successfully optimized, and the enantiomeric distribution of the most abundant optically active compounds were revealed. A clear and scented cannabis oil rich in terpene and terpenoid compounds was produced demonstrating that MAHD technology offers remarkable advantages in term of operational simplicity and cost. At the same time, it is worth empathizing the ecological aspects of the methodology according to green chemistry principles such as minimizing toxicity, waste production and saving energy.

[1] L. Calvi, D. Pentimalli, S. Panseri, L. Giupponi, F. Gelmini, G. Beretta, D. Vitali, M. Bruno, E. Zilio, R. Pavlovic et al., *J. Pharm. Biomed. Anal.* **2018**, 150, 208-219.

"Cholesterol is not considered a nutrient of concern for overconsumption" (Dietary Guidelines for Americans 2015)

D. Naviglio[1], D. Montesano[2], M. Ciaravolo[1], A. Savastano[1], V. Nebbioso[1], M. Gallo[3]

[1]Department of Chemical Sciences, University of Naples Federico II, via Cintia, 4, 80126 Naples, Italy; [2]Department of Pharmacy, University of Naples Federico II, via D. Montesano 49, 80131 Naples, Italy; [3]Department of Molecular Medicine and Medical Biotechnology, University of Naples Federico II, via Pansini, 5, 80131 Naples, Italy.

Chicken egg is one of the most complete natural foods from a nutritional point of view, as it provides the most important macronutrients for human nutrition: proteins, mainly in the yolk, but also in the egg white, fats mainly in the yolk, few carbohydrates, vitamins and minerals. However, it has been considered a major dietary source of cholesterol [1] and for this reason it has been limited for human intake to a maximum of two eggs per week. Early research to determine the cholesterol content in eggs resulted in a result of 274 mg / egg. These data have been used for several years as the absolute cholesterol content in eggs. The 2015-2020 Dietary Guidelines for Americans [2] recommended the consumption of eggs as part of a healthy diet and have abolished the dietary cholesterol intake limit of 300 mg/day in the American dietary guidelines valid since 1968. Already in 2001 Naviglio et al. focused their attention on cholesterol content in eggs [3,4] and they highlighted, on the basis of results about cholesterol content in eggs, that assumption of two eggs a day were not a concern for healthy individuals. In literature, after 2015, several articles report that healthy subjects who were asked to eat one or more eggs a day for three to four weeks were subsequently monitored for their blood cholesterol level. At the end of the test, the results showed that the cholesterol content in the blood had not changed. Finally, there are therefore no contraindications to the intake of two eggs a day for healthy individuals [5,6].

[1] D. Naviglio, A. Battaglia, A. De Vito, C. Raia, L. Schiavo and R. Romano, *Avicoltura Ricerca* **2002**, 71(2), 35-41.

[2] U.S. Department of Health and Human Services and U.S. Department of Agriculture. 2015–2020 dietary guidelines for Americans. Available at: https://health.gov/dietaryguidelin es/2015/guide lines/.

[3] D. Naviglio, R. Romano, L. Schiavo, F. De Gaetano, A. Battaglia, M. Ugliano, *Riv. It. Sost. Grasse* **2001**, 78, 117-126.

[4] D. Naviglio, M. Gallo, L. Le Grottaglie, C. Scala, L. Ferrara, A. Santini, *Food Chemistry* **2012**, 132, 701-708.

[5] D. Naviglio, C. Langella, S. Faralli, M. Ciaravolo, M.M. Salvatore, A. Andolfi, V. Varchetta, R. Romano, M. Gallo, *Foods* **2018**, 7, 131.

[6] D. Naviglio, *Med. Chem.* **2018**, 6, 040.

A rapid analytical method for the determination of 45 elements in extra-virgin olive oils

Maria Luisa Astolfi[a], Giulia Vitiello[a], Elisabetta Marconi[b]

[a] Department of Chemistry, Sapienza University, Piazzale Aldo Moro 5, I-00185 Rome, Italy; [b] Institute of Atmospheric Pollution Research, National Research Council (CNR), Via Salaria Km 29,300, Monterotondo St., 00015 Rome, Italy

The accurate determination of trace elements in edible olive oils is still an analytical challenge due to their low concentration levels and the complex matrix of vegetable oils. However, the study of possible chemical contaminants and their levels in edible olive oils is a research priority for preserving the high nutritional value and the high organoleptic quality of these products [1]. Furthermore, the analysis of trace elements plays an important role as a basis for oil adulteration detection and oil quality control.

This study evaluates a new method to miniaturize the sample digestion for extra virgin olive oils by inductively coupled mass spectrometry (ICP-MS) in order to achieve accurate and reproducible results with low detection limits for the analyzed trace elements. This method has been designed to carry out the sample preparation and instrumental analysis from a single tube to prevent sample loss, minimize contamination and reduce volumes of acid and the required final dilution. To evaluate the best and fastest sample preparation procedure, ultrasonic extraction and wet digestion methods were compared using oil certified reference material with different reagent mixtures, reagent volumes, and times for sample extraction or digestion. The use of 5 mL reagent mixture consisting of 10% (v/v) HNO_3 and H_2O_2, 2:1 (v/v) for sample digestion in a water bath (95 °C, 40 min) was found to produce satisfactory results in all cases as validated from sample recovery experiments over three different extra virgin olive oil samples [2]. This method can be used for applications such as routine analysis with high sample throughput and geographical traceability.

.

[1] C. Cabrera Vique, P.R. Bouzas, M.J. Oliveras López, *Food Chem.* **2012**, *134*, 434–439.
[2] M.L. Astolfi, E. Marconi, G. Vitiello, L. Massimi, *Food Chem.* **2021**, *360*, 130027.

Innovative spectroscopic approach for bloodstains identification

Laura Barone [a], Giuseppina Gullifa [a], Stefano Materazzi [a], Roberta Risoluti [a]

[a] *Department of Chemistry – "Sapienza" University of Rome p.le A.Moro 5, 00185, Rome, Italy*

Blood is the most studied biological evidence in forensic investigations. Its detailed analysis is necessary to confirm first of all its origin and then it would be advantageous to detect and characterize it, with the same accuracy, on different surfaces. This work, aims to implement a new analytical platform based on MicroNIR spectroscopy combined with chemometrics for the identification of bloodstains on different substrates.

Spectroscopic techniques proved to be promising in characterizing complex matrices and offered the advantages to be easy-to-use and non-destructive without requiring any pretreatment. This would avoid contamination of the sample for subsequent confirmatory analysis with the reference official procedure. In addition, the coupling with chemometric tools will allow for multivariate statistical analysis which provides models of prediction for qualitative response with the required accuracy.

The innovation of this approach consists in an ultra-compact and portable device operating in the Near Infrared region, totally controlled via Bluetooth to a laptop. The peculiarity of the portable NIR analytical approach is to bring the laboratory to the "field" obtaining results quickly, since the acquisition time and the instrumental response require only few seconds. In addition, the reduction in size does not compromise the performance of the instrument, allowing results comparable to those obtained in the laboratory.

The platform is entirely developed with the aim of simplifying the identification of bloodstains and to facilitate the rapid interpretation of results, as once the model is assessed, it could be used to process real samples in a "click-on" device. All the experiments were carried out with the aim of developing a model of prediction as robust as possible. Variability of the spectroscopic signal as a function of the matrix effect of blood was taken into consideration and the interferences due to the complexity of the matrix were considered by evaluating a pool of samples. Principal Component Analysis (PCA) and Partial Least Square-Discriminant Analysis (PLS-DA) allowed to discrimate bloodstains from substances identified commonly as false positives on different surfaces. Next, we will evaluate the capabilities of the MicroNIR-Chemometrics platform to verify the ability to discriminate without classification errors. The latter will have to be sensitive and accurate to be used as a first level test in forensic science, and allow to screen suspicious samples for confirmatory analysis using reference procedures.

[1] Risoluti, R., Gullifa, G., Battistini, A. & Materazzi, S. *Analyst* **145**, 1777–1782 (2020).

[2] Kumar, R., Sharma, K. & Sharma, V. *Sci. Justice* **60**, 538–546 (2020).

[3] Risoluti, R., Gullifa, G., Battistini, A. & Materazzi, S. *Talanta* **211**, 120672 (2020).

Surface characterization of CuZn37 alloys in contact with artificial saliva: the role of organic compounds

Deborah Biggio[a], *M. Fantauzzi*[a], *B. Elsener*[a], *A. Rossi*[a],

[a] *Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, 09042 Cagliari, Italy;*

Copper and copper alloys have numerous applications due to their workability and durability. In the case of copper-zinc alloys in contact with an aqueous environment or with biological fluids, for example saliva [1], the formation of a thin layer of corrosion products (called *patina*) is important for the stability of these alloys in contact with the environment. The corrosion behaviour of CuZn37 brass alloy, exposed for 1 hour to Darvell (D), [2] Carter – Brugirard (CB) [3] and SALMO (S) [4] saliva formulations (Tab.1) has been studied by means of electrochemical measurements, open circuit potential (OCP) and the polarization resistance (Rp) measurements. Our recent study [6] has shown that the dissolution mechanism of the alloy CuZn37 in the artificial saliva solutions is under anodic control. Moreover, the corrosion rate (µm/year) varies in that order: Darvell > Carter-Brugirard > SALMO. This work focuses on X-Ray Photoelectron Spectroscopy (XPS) surface analysis in order to evaluate the effect of the different model solutions on the corrosion and compare them with the data previously obtained with the Tani-Zucchi solution [1,5]. The XPS S2p high -resolution spectra (Fig.1) show on all samples the presence of a sulfur signal at 163.7 (0.1) eV assigned to SCN^-. A phosphorus P 2p signal at 134.5 (0.1) eV attributed to a phosphate was revealed on the surface of the brass exposed to SALMO's and Carter-Brugirard's formulation. On the surface of the brass alloy exposed to Darvell's formulation, the phosphate signal is absent. Instead, another component is revealed in the S 2p signal at 162.5 (0.2) eV (Fig. 1) attributable to sulphide. These data suggest that the presence of simultaneous equilibria due to the presence of different organic compounds in Darvell's formulation could cause the selective dissolution of Zinc (dezincification). The formation of soluble zinc complexes (e.g. zinc citrate) might limit the formation of insoluble protective species such as zinc-phosphate which was observed on the surface of the brass alloys in contact with SALMO and Carter-Brugirard saliva, which contain urea as principal organic compounds, as well as Tani-Zucchi saliva.

Anions	**Concentration (mmol / dm^3)**		
	D	**CB**	**S**
Cl^-	30.1	28.0	17.6
$H_2PO_4^-$ & HPO_4^{2-}	4.7	3.5	8.5
HCO_3^-	7.1	18.0	11.4
SCN^-	2.5	3.4	2.0
F^-	-	-	0.0025
Organics	1.3 (Citrate, lactic acid, urea, uric acid)	2.2 (Urea)	3.7 (Urea, glycine)

Tab.1: Artificial saliva formulations: Darvell (D); Carter-Brugirard (CB); SALMO (S).

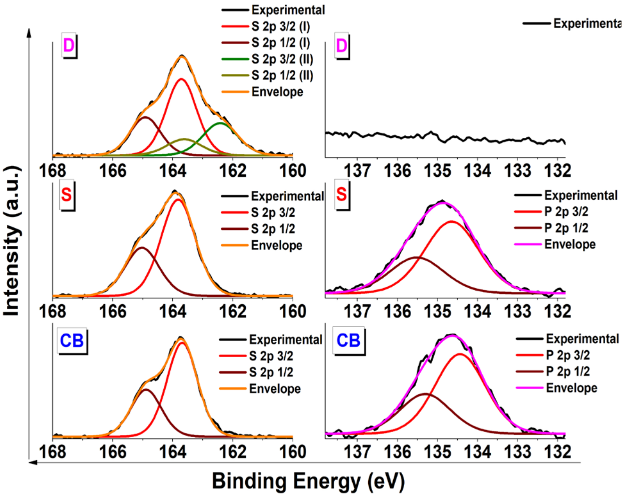


Fig.1: High-Resolution spectra (left S 2p; right P2p) of Cu37Zn after 1h in contact with artificial saliva: Darvell (D), SALMO (S), Carter-Brugirard (CB).

[1] Cocco F., Fantauzzi M., Elsener B., Rossi A., *Rsc Advances* **2016**, 6, 90654.
[2] Darvell B.W., *Journal of Oral Rehabilitation*, **1978**, 5, 41.
[3] Vitelaru C.,et al., *M. Science and E. Technology*, **2014**, 45, 91.
[4] Crea F.,et al., *Bioinorganic Chem. and Applications*, Volume **2015**.
[5] Tani G., Zucchi F., *Minerva Stomatologica*, **1967**, 16, 710.
[6] D. Biggio, *Master's thesis,* **2019**.

A multi-analytical approach for the study of immortalized hippocampal neurons after mild heat shock

[a,b] Angela Gilda Carota, [a] Beatrice Campanella, [c] Laura Colombaioni, [a] Massimo Onor, [a] Stefano Legnaioli, [a] Emilia Bramanti

[a] Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici (CNR-ICCOM), Pisa; [b] Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Pisa [c] Consiglio Nazionale delle Ricerche, Istituto di Neuroscienze (CNR-IN), Pisa.

The accurate *in vitro* analysis of the metabolomic profiles of cell lines has definitely proved to have numerous pharmacological and medical applications, with several advantages if compared to the use of animal models or human subjects.

Among cell lines, immortalized hippocampal neurons HN9.10e represent a reliable model of one of the most vulnerable regions of the central nervous system. This study is a further development of a previous investigation, where the extracellular metabolic profile of HN9.10e was defined under standard conditions [1]. Here both the behavior and the level of low-molecular weight metabolites of HN9.10e were studied after a minimal perturbation of the cell system, which was heated at mild temperatures. Confocal microscopy, liquid chromatography coupled with diode array detection, µ-Raman and FT-IR spectroscopy were used in combination with a chemometric approach. The rationale behind these experiments is that even subcritical conditions could result in detectable cellular impairment. The biological relevance of the results is given by the monitoring of the metabolic trajectory related to the complete neuronal compensation of a sub-lethal damage.

[1] B. Campanella, L. Colombaioni, R. Nieri, E. Benedetti, M. Onor, E. Bramanti, *Frontiers in chemistry* **2021**, 9.

Ultrasensitive plasmonic assay and specifically-designed PNA probes for circulating microRNAs detection: towards a liquid biopsy approach

R. D'Agata,[a] *N. Bellassai,*[a] *M.C. Giuffrida,*[b] *A. Rozzi,*[c] *A. Finotti,*[d] *G. Gasparello,*[d] *R. Corradini,*[c] *R. Gambari,*[d] *J. Dostalek,*[e] *W. Knoll,*[e] *G. Spoto* [a,b]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Italy*
[b] *Consorzio Interuniversitario "Istituto Nazionale di Biostrutture e Biosistemi", c/o Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Italy*
[c] *Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, Italy*
[d] *Dipartimento di Scienze della vita e Biotecnologie, Università di Ferrara, Italy*
[e] *AIT-Austrian Institute of Technology GmbH, Konrad-Lorenz-Strasse 24, Tulln 3430, Austria*

Recently, circulating microRNAs (miRNAs), detected in serum and plasma, have been associated with a range of different tumor types, making them particularly attractive as non-invasive diagnostic markers in cancer. However, several properties of miRNAs, such as their short size and low concentration in biofluid, are crucial features to developing the diagnostic assay based on liquid biopsy [1]. We report a sensitive, versatile and multiplexed plasmonic platform to detect miRNAs cancer biomarkers directly in human plasma as a liquid biopsy approach. The platform implies an assay configuration involving specifically-designed (*T-linker*) PNA probes [2] to overcome the challenges for miRNAs analysis. The PNA probe geometry provides an amended surface environment for PNA/miRNA interaction compared to vertical immobilization of (*C-linker*) PNA. Once hybridized with the probe, both the 3' and 5' ends of miRNA may be available for the assay's following steps. The fine-tuning of PNA probe orientation and its surface density was investigated for the first time, by Surface Plasmon Fluorescence Spectroscopy (SPFS) [3] and Surface Plasmon Resonance Imaging (SPRI) [4] to optimize the functionalization and specificity of miRNAs detection. The close proximity to the sensor surface of *T-linker* PNA then translated the detection limit to one femtomolar (fM) with the readout based on the nanoparticle-enhanced SPRI. The platform provides appealing features for determining clinically relevant miRNAs (i.e., miR-141 and miR-221) [5] as examples of circulating biomarkers of solid tumors such as glioma and colorectal cancer, and non-solid tumors such as leukaemia (miR-210). The plasmonic bioassay detects miRNAs directly in a relatively low amount of total RNA from circulating tumor cells with a wide linear response range (4 orders of magnitude) and high selectivity. Moreover, the newly designed biosensor quantifies circulating miRNA directly in the plasma of colorectal cancer patients. The new diagnostic tool offers an efficient, cost-effective and straightforward analysis to detect relevant biomolecules for an early cancer diagnosis, with sensitivity down to fM range, avoiding plasma sample manipulation that may produce misleading results, and expanding the potential of personalized cancer.

[1] R. D'Agata, G. Spoto, *Anal. Bioanal. Chem*. **2019**, *411*, 425.
[2] A. Manicardi, A. Rozzi, S. Korom, R. Corradini, *Supramol. Chem*. **2017**, *29*, 784.
[3] D. Kotlarek, F. Curti, M. Vorobii, R. Corradini, M. Careri, W. Knoll, C. Rodriguez-Emmenegger, J. Dostálek, *Sens Actuators B Chem*, **2020**, *320*, 128380.
[4] R. D'Agata, N. Bellassai, M. Allegretti, A. Rozzi, S. Korom, A. Manicardi, E. Melucci, E. Pescarmona, R. Corradini, P. Giacomini, G. Spoto, *Biosens. Bioelectron*. **2020**, *170*, 112648.
[5] A. Finotti, M. Allegretti, J. Gasparello, P. Giacomini, D.A. Spandidos, G. Spoto, R. Gambari, *Int J Oncol*. **2018**, *53*, 1395.

Identification and quantification of toxic compounds and essential molecules in the context of tuna fishery industry waste valorization

Danilo Donnarumma[a], Roberta La Tella[b], Federica Vento[a,b], Francesca Rigano[b], Luigi Mondello[a,b,c,d]

[a]*Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

[b]*Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

[c]*BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

[d]*Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy*

The tuna processing industry generates a very large amount of waste, since less than 50% of the raw material is destined for human consumption, e.g. used for the production of canned foods, thus generating the complete loss of high-value biomolecules such as bio-peptides, omega-3 fatty acids, essential amino acids, essential metals, and vitamins. Due to the synergic effect of all these compounds, fish is a well-known functional food since it can contribute to the reduction of chronic diseases and to the general well-being of the organism, according to both a therapeutic and preventive approach. On the other hand, by focusing on metals or amino acids, tuna is considered potentially toxic due to its level of heavy metals (e.g. mercury), proportional to its size, and the high content of histidine, which could be converted into histamine, if the fish is subjected to an incorrect storage, responsible for histamine intoxication, also known as scombroid syndrome. Histamine is odorless and tasteless, therefore poisoning can occur without deterioration of the fish being perceptible from an organoleptic point of view, only the laboratory test is able to reveal the presence of toxic levels.

In this work, Yellowfin tuna (*Thunnus albacares*) was used as a model for fish processing by-products, as it is a large epipelagic species widely distributed in the tropical and subtropical waters of the major oceans. Inductively coupled plasma - mass spectrometry (ICP-MS) and a fast gas chromatographic – mass spectrometry (GC-MS) methods were validated and applied for the determination and quantification of metals and free amino acids (histamine included), respectively. The methods developed and validated in this work can be of potential interest for the analysis of by-products deriving from various food processing industries, paving the way for the reutilization of such wastes as a primary resource in a new production cycle.

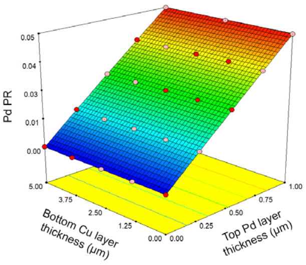
Film thickness determination of metal multilayers by XRF multivariate analysis using Monte Carlo simulated standards

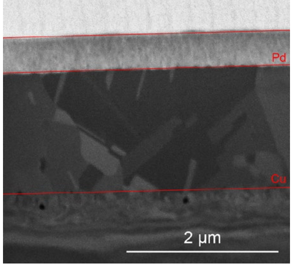
<u>Walter Giurlani</u> [a,b], Martina Vizza [a], Stefano Mauro Martinuzzi [a,b,d], Lorenzo Fabbri [a], Roberta Emanuele [a,b], Federico Pizzetti [a], Andrea Comparini [a], Enrico Berretti [c], Alessandro Lavacchi [c], Massimo Innocenti [a,b,c,d]

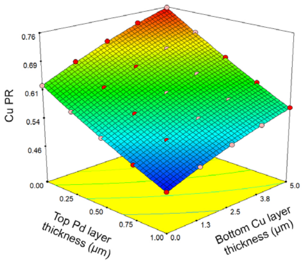
[a] Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [b] National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy; [c] Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy; [d] Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto F.no (FI), Italy;

Metal thin films are present in many scientific, technological and industrial applications and the thickness determination is a fundamental aspect that have to be characterized. Among the numerous techniques for the thickness determination none allows fast, inexpensive and non-destructive analysis [1]. In this study we focused on electroplating industry application, where the coatings vary between 50 nm and 10 µm. Even if X-Ray Fluorescence spectroscopy (XRF) is a widespread technique in this field, the thickness determination of multilayer coatings is not straightforward because of the complex physics involved and the high matrix effects. Errors exceeding 10% are typical but not always acceptable. XRF quantification is based on the Fundamental Parameters (FP) approach, sometimes adjusted with empirical measurements. Due to the difficulties in the standards preparation certified samples are used but with two major drawbacks: (i) there is not the availability of standards for any possible coating composition and architecture and (ii) commercial standard are quite expensive. In this work, we used a semiquantitative approach for the coating thickness measurement based on the construction of calibration curves through simulated XRF spectra obtained with Monte Carlo algorithm. Multivariate data analysis was performed to consider the effect of the multilayer structure simultaneously [2]. Simulations have been performed with the software XMI-MSIM [3]. We assessed the accuracy of the method by comparing the results with XRF-FP and FIB-SEM analysis. The results show good quantitative values even without the use of any standard with known thickness.

The authors acknowledge Regione Toscana POR CreO FESR 2014-2020 – azione 1.1.5 sub-azione a1 – Bando 1 "Progetti Strategici di ricerca e sviluppo" which made possible the projects "ACAL 4.0" (CUP 3553.04032020.158000165_1385), "A.M.P.E.R.E." (CUP 3553.04032020.158000223_1538), "GoodGalv" (CUP 3647.04032020.157000060) and "GIGA 4.0" (CUP 3553.04032020.158000105_1242).







[1] W. Giurlani, E. Berretti, M. Innocenti, A. Lavacchi, *Coatings* **2020**, *10*, 1211.
[2] W. Giurlani, E. Berretti, A. Lavacchi, M. Innocenti, *Anal. Chim. Acta* **2020**, *1130*, 72.
[3] T. Schoonjans, V.A. Solé, L. Vincze, M. Sanchez Del Rio, K. Appel, C. Ferrero, *Spectrochim. Acta - Part B At. Spectrosc.* **2013**, *82*, 36.

2014 2020 POR CreO REGIONE TOSCANA FONDO EUROPEO DI SVILUPPO REGIONALE
Unione Europea Fondo Europeo di Sviluppo Regionale
REPUBBLICA ITALIANA
Regione Toscana

Low-cost miniaturized NIR spectrometer as an analytical tool for monitoring kefir fermentation process

Giulia Gorla[a], Sara Fumagalli[a], Marleen Huisman[b], Carlo Bertinetto[b], Jeroen J. Jansen[b], Barbara Giussani[a]

[a]Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Via Valleggio 9, 22100 Como, Italy
[b] Institute for Molecules and Materials (Analytical Chemistry), Radboud University, Nijmegen, The Netherlands

Kefir is a dairy product with raising interest due to its health beneficial effects. It can be prepared from different milk types via fermentation inoculating milk with kefir grains. Starting from milk, several metabolic products like lactic acid, ethanol, carbon dioxide, and aroma compounds are generated to make the distinguishable flavour and aroma of kefir [1].

During the last decades, NIR spectroscopy has been largely proved as an effective tool for process analytical control of different food fermentation such, for instance, wine, beer and yoghurt production [2]. In recent years, miniaturized NIR spectroscopy has gained extensive interest due to the rapidity, portability and possible uses with low or absent samples pretreatment. Applications in the food industry have been demonstrated with consistent results in comparison with benchtop instrument primarily regarding quantification of macronutrients and identification of adulterants [3].

In this study, a low-cost miniaturized spectrometer with a spectral range between 1350 and 2550 nm was tested with several acquisition strategies to follow kefir fermentation. Semi-skimmed cow milk was chosen as fermentation media. The spectra acquired, in combination with multivariate analysis, were used to control the fermentation advances. The potentialities and the difficulties in applying the miniaturized spectrometer on a heterogeneous liquid sample to monitor its physico-chemical changes over time were investigated obtaining satisfactory results.

[1] Farag, M.A.; Jomaa, S.A.; Abd El-Wahed, A.; R. El-Seedi, H., *Nutrients* **2020**, *12*, 346.
[2] Jan U. Porep, Dietmar R. Kammerer, Reinhold Carle, *Trends in Food Science & Technology*, **2015**, 46, 211-230.
[3] Beć, KB, Grabska, J, Huck, CW. *Chem Eur J* **2020**; 27: 1514–1532.

XAS study of Manganese Hexacyanoferrate cathode material in aqueous Zn-ion batteries at three K-metal edges

Min Li[a], Rosalinda Sciacca[a], Mariam Maisuradze[a], Giuliana Aquilanti[b], Jasper Plaisier[b], Mario Berrettoni[c], Giorgetti Marco[a]

[a] Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy; [b] Elettra - Sincrotrone Trieste, s. s. 14, km 163.5, Basovizza 34149, Trieste, Italy; [c]School of Science and Technology, Chemistry Division, University of Camerino, Camerino, Italy

Manganese hexacyanoferrate (MnHCF) has attracted widely attention as promising cathode material, owning to its low cost, environmental friendly, and high specific capacity and voltage plateau [1-3]. Here, the electrochemical performance of MnHCF was studied in aqueous Zn-ion batteries (ZIBs). By using the strong selectivity of the X-ray absorption spectroscopy (XAS) for the atomic species we have recorded and analyzed three different metal K-edges, revealing their local geometric and electronic structure in a set of ex-situ electrodes. From Fe K-edge spectra, no obvious change was observed from different charge/discharge state samples, and this indicates that there is no apparent change for the local Fe-sites environment. However, the XAS spectra of Mn K-edge shown apparent change after 10 cycles. The result also showed a -Zn-NC-Fe- structural framework in the cycled samples, and this indicates that Zn partially replaced Mn upon cycling, resulting in a dissolution the Mn-sites. A gradually activation of Fe-sites at beginning cycles was observed, which can attribute to the alleviate spatial resistance with the dissolution of Mn-sites, and the substitution Mn-sites by non-active Zn can explained the decreasing of capacity after the activation process.

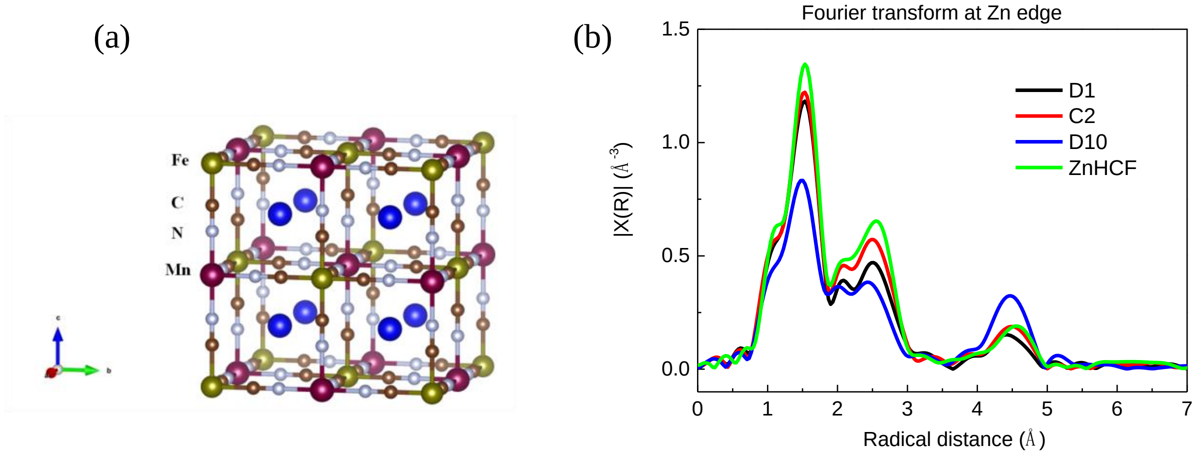


Figure 1 (a) crystal structure model of MnHCF; (b) Fourier transform (FT) of Zn K-edge k^2-weighted EXAFS signal.

[1] A. Mullaliu, J. Asenbauer, G. Aquilanti, S. Passerini, M. Giorgetti. *Small Methods*. **2019**, 1900529.
[2] L. Ma, Sh. Chen, Ch.Long, X. Li, Y.Zhao, Zh. Liu, Zh. Huang, B. Dong, J. Zapien, Ch.Zhi. *Energy Mater*. **2019**, 1902446.
[3] Q. Li, K. Ma, G.Yang, Ch. Wang. *Energy Storage Materials*, **2020**, 29, 246-253.

Analytical characterization of laser-ablated silver nanoparticles for safe and biodegradable food packaging applications

M.C. Sportelli[a, b], *A. Ancona*[b, c], *A. Volpe*[b, c], *C. Gaudiuso*[b, c], *V. Lavicita*[d], *A. Conte*[d], *M.A. Del Nobile*[d], *V. Miceli*[e], *N. Cioffi*[a, f]

a. *Chemistry Department, University of Bari, Via Orabona, 4-70126 Bari, Italy*
b. *IFN-CNR, Physics Department, University of Bari, Via Amendola, 173-70126 Bari, Italy*
c. *Physics Department, University of Bari, Via Orabona, 4-70126 Bari, Italy*
d. *Department of Agricultural Sciences, Food and Environment, University of Foggia, Via Napoli 25-71122 Foggia, Italy*
e. *ENEA Research Center, BIOAG division - ss Appia km 700 – 72100 Brindisi, Italy*

f. *CSGI (Center for Colloid and Surface Science) c/o Chemistry Department, University of Bari, Via Orabona, 4-70126 Bari, Italy*

The application of metals in the form of nanostructured antimicrobials is continuously expanding. In the last decades, especially Ag-based nanoantimicrobials [1] have attracted the interest of scientists, as assessed by the huge number of reports on their synthesis and characterization [2]. Designing bioactive materials, with controlled metal ion release, exerting significant biological action and associated to low toxicity for humans, is nowadays one of the most important challenges for our community. The most looked-for nanoantimicrobials are capable of releasing metal species with defined kinetic profiles, either slowing down or inhibiting bacterial growth and pathogenic microorganism diffusion. In recent years, we have developed and deeply characterized many different nanoantimicrobial systems, ranging from Ag-modified textiles to bioactive food packaging [3]. On the one hand, all these materials were found to be human safe since they showed no significant leaching of (potentially toxic) whole nanoparticles into contact media. On the other hand, antibacterial ionic species released by transition metal nanophases provided a powerful alternative route to fight bacterial resistance towards conventional antibiotics and disinfecting agents. Laser ablation synthesis in solution (LASiS) has been used in our labs to produce bioactive Ag-based nanocolloids, in isopropyl alcohol, which can be used as water-insoluble nano-reservoirs in composite materials [4]. In fact, including nanophases into polymers (like polyethylene oxide or poly(3-hydroxybutyrate-co-3-hydroxyvalerate)) allows to produce multifunctional packaging, combining biodegradable and antibacterial properties of both organic and inorganic phases [5]. In this study, infrared spectroscopy was used to evaluate the chemical state of pristine nanoparticles and final materials, providing useful information about synthesis processes, as well as storage and processing conditions. Transmission electron microscopy was exploited to study morphologies of nano-colloids, along with UV-Vis for bulk chemical characterization. Electrothermal atomic absorption spectroscopy was used to investigate metal ion release from modified surfaces and industrial products. Analytical spectroscopy results were matched with bioactivity tests on target microorganisms of food spoilage. Different approaches to the synthesis and characterization of 2nd-generation nanoantimicrobials, e.g., to those materials combining antibacterial efficiency and nanosafety issues, will be critically discussed, based on spectroscopic, morphological, release and bioactivity evidence.

References:

[1] M.D. Dizaj et al., Mat. Sci. Eng. C (2014), 44, 278–284.
[2] M.C. Sportelli et al., TrAC (2016), 84A, 131-138.
[3] M.C. Sportelli et al., Applied Surface Science (2020), 507, 145156.
[4] M.C. Sportelli et al., Food Pack. Shelf Life (2019), 22, 100422.
[5] S. Raho et al., Foods (2020), 9, 1459.

SAFER Smart Labels at work on fish

Lisa Rita Magnaghi [a,b], *Clelia Sarta* [a], *Camilla Zanoni* [a], *Giancarla Alberti* [a], *Paolo Quadrelli* [a,b]
and Raffaela Biesuz [a,b]

[a] *Dipartimento di Chimica, Università di Pavia, via Taramelli 12, 27100 Pavia, Italy;*
[b] *Unità di Ricerca di Pavia, INSTM, Via G. Giusti 9, 50121-Firenze, Italy*

In recent decades, the interest in systems able to detect food degradation, giving a quick response, simple to be read, and suitable for implementation in control systems and smart labels has increased continuously. We developed and proposed miniaturized optical sensors to assess the meat spoilage, monitoring the change of headspace byproducts developed over the meat. Different types of proteinaceous foods have been tested. We demonstrated that the colour changes follow the real volatilome changes related to the degradation process provoked by microbial activity inside the meat. [1-2]

More recently, we developed sensors where the receptors, i.e. sulphonphtalein indicators, are permanently fixed in the EVOH matrix. [3] The labels developed are known as SAFER Smart Labels. In the present investigation, focused on fishes, *o*-cresol red has been selected and used in two forms, as described in [4]. See Fig 1 (a). Among the proteinaceous food, fish is possibly the most perishable. The reason is related to the fish metabolism, which differs from that of land vertebrates, having the extraction system mainly through gills and skin. That is why the fresh fish has a fishy odour, and it explains why simple BAs are found in the headspace, differently from other types of meats [4].

The colour evolution of the two sensors was expressed as the variation of the average RGB triplets during the storage of five different fishes (codfish, swordfish, gurnard fish, flounder, redfish). The best sensors in term of thickness were selected. As an example, in Fig 1 (b), the case of swordfish fillet is shown. A PCA model to follow the degradation pattern was obtained for each type of fish from RGB triplets. In all cases, it is possible to identify an intermediate step and, very clearly, the last dangerous degradation step. External samples were used to be projected into each model. Finally, the different fishes' patterns were summarised by three-way PCA. The present investigation confirms that the evolution of sensors colour follows all the spoilage steps. Moreover, it can be followed by the naked eye, and a reliable label, as reported in Fig 1 (c), can be developed.

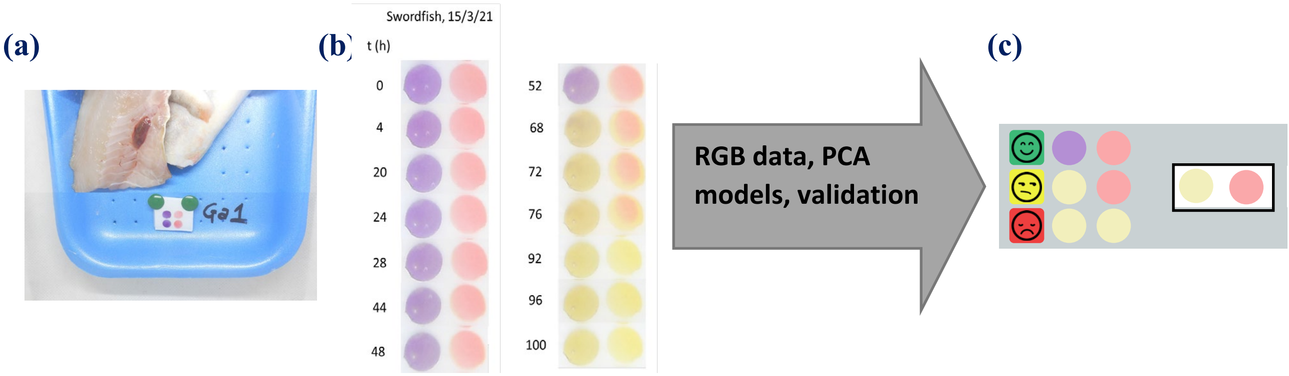


Figure 1: (a) Fish sample with sensors, **(b)** Colour evolution during for swordfish sample stored in the domestic fridge **(c)**. final intelligent label prototype.

[1] L. R. Magnaghi et al J. Agric. Food Chem. 2020, 68, 45, 12702–12709
[2] L. R. Magnaghi, et al. J. Agric. Food Chem. 2020, 68, 45, 12710–12718
[3] R. Biesuz et al. Sensors for the Evaluation of the Quality of Meat-Based Food. WIPO PCT/IB2020/052998. March 30, 2020.
[4] R. Biesuz and L.R. Magnaghi. Chapter of Meat and Nutrition book. DOI: doi.org/10.5772/intechopen.96279

Liquid phase exfoliated Transition Metal Dichalcogenides for gas sensing

Sara Gaggiotti[1], Flavio Della Pelle[2], Annalisa Scroccarello[2], Angelo Cichelli[1], Dario Compagnone[2]*

[1] *Department of Medical, Oral and Biotechnological Sciences, "G. d'Annunzio" University Chieti-Pescara, Via dei Vestini 31, 66100 Chieti, Italy*
[2]*Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Campus "Aurelio Saliceti" via R. Balzarini 1, 64100 Teramo, Italy.*

Fast gas sensing is become strategic in modern society to monitoring environmental pollutants, identify safety and process markers in food, and also analyze human breath for rapid medical diagnostic.

Different sensing elements have been employed to equip gas sensors, to allow specific target analysis, or to maximize the response information in gas sensors arrays. In this regard, the use of peptides, DNA, conducting polymers, molecularly imprinted polymers, carbon nanotubes, and metal oxides have been widely reported [1]. A fundamental feature, which influences the choice of the sensing elements, is the working conditions in which the sensor needs to be used since often sensors need high operating temperature (e.g., MOS) or are affected by environmental humidity (e.g., conductive polymers) [2].

Nanomaterials have been widely used as sensing elements or to hosting sensing elements for gas sensors, between these Transition Metal Dichalcogenides (TMDs), have been quite explored. However, to the best of our knowledge, the TMDs use on Quartz-crystal microbalances (QCM) based gas sensors are still understudied. TMDs properly exfoliated results in 2D-few layer sheets with high surface to volume ratio, characterized by intrinsic chemistry correlated to the native metal and chalcogen atom; the exfoliation route strongly influences the final material conformation and surface chemistry, thus potentially affecting/modulating the sensing ability [3].

In this work we present, a systematic study where Group VI TMDs (MoS_2, $MoSe_2$, WS_2, WSe_2) were exfoliated in water, using liquid-phase exfoliation (LPE) assisted by natural molecules as stabilizing agents. The TMDs exfoliation has been attempted taking advantage of three natural phenolic compounds (Ellagic acid, Tannic acid, and Catechin) and a widely used surfactant, namely, sodium cholate. The LPE allowed producing 2D nanosheets with a few layers of thickness.

The 16 different TMDs nanoflakes obtained, have been characterized and used to modify QCMs, placed in a gas sensor array (e-nose), and challenged for the detection of different volatile organic compounds (VOCs) belonging to different chemical classes (i.e., alcohols, esters, ketones, aldehydes, and terpenes). Finally, 12 TMDs were selected, maximizing the response variability towards target VOCs, and successfully used to evaluate the banana aroma evolution during post-harvest ripening.

As hypothesized, the TMDs sensing ability resulted modulated by the nanomaterial's different composition and by the stabilizing agent used, that act as a modulating agent able to influence the gas sensor affinity towards different VOCs. Moreover, high TMDs affinity variability allows the implementation of a gas sensor array able to monitoring food aroma evolutions in real matrices. In conclusion, for the first time, has been demonstrated of TMDs exfoliated by using different natural compounds can act as useful elements for gas sensing in common environmental conditions.

References

[1] S. Gaggiotti, F. Della Pelle, M. Mascini, A. Cichelli, D. Compagnone *Sensors.* **2020**, 20(16), 4433.

[2] Y. F. Sun, S. B. Liu, F. L. Meng, J.Y. Liu, Z. Jin, L.T. Kong, J.H. Liu *Sensors.* **2012**, 12(3), 2610-2631

[3] D. Rojas, F. Della Pelle, M. Del Carlo, D. Compagnone, A. Escarpa Electrochem. Commun. **2020,** 115, 106718

A clover-like paper biosensor for mercury (II) on-site monitoring with a combined bioluminescent-colorimetric detection

Laura Montali[a,b], *Antonia Lopreside*[a,b], *Maria Maddalena Calabretta*[a,b] *and Elisa Michelini*[a,b]

[a]*Department of Chemistry "Giacomo Ciamician", University of Bologna, Via Selmi 2, 40126 Bologna, Italy*
[b]*Centro di Ricerca Biomedica Applicata (CRBA), Azienda Ospedaliero-Universitaria Policlinico S. Orsola-Malpighi, Bologna, Italy*

In recent years it is becoming increasingly important to monitor mercury and its compounds since, due to its persistence and ability to bioaccumulate in the environment, truly alarming levels of contamination have been reached. Mercury is one of the most widespread toxic heavy metals found in water, air and food. The availability of rapid and sensitive biosensors to monitor mercury is thus a priority.

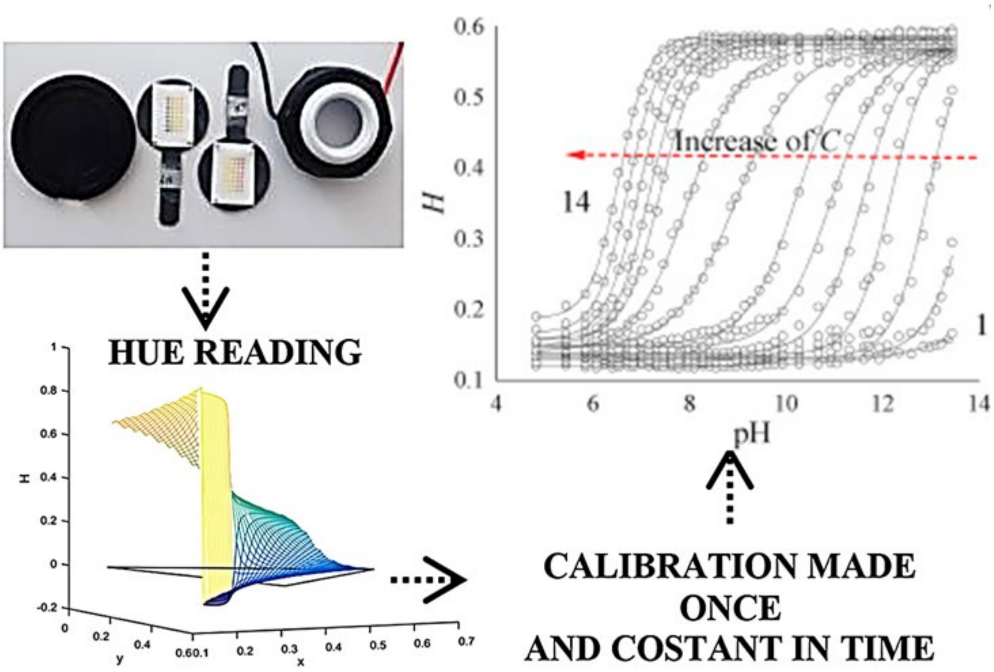
We developed the first low-cost paper biosensor integrating bioluminescent and colorimetric detection with a smartphone. This biosensor is composed of a three-leaf sensing paper which exploits an orthogonal detection of mercury (II) by combining three different biorecognition principles and different signal outputs: i) bioluminescent detection with a mercury-specific *E. coli* bioreporter strain, ii) colorimetric detection with a purified β-galactosidase enzyme which is irreversibly inhibited by mercury and other toxic heavy metal ions reacting on the sulfhydryl group of cysteine, and iii) a spontaneously bioluminescent *V. fischeri* strain which is used to quantitatively assess sample toxicity and correct the analytical signal accordingly. All the three sensory elements and substrates, furimazine for the *E. coli* bioreporter strain and chlorophenol red-β-D-galactopyranoside for colorimetric detection of β-galactosidase, were integrated in a paper sensor via different immobilization methods to provide a stable all-in-one disposable cartridge. This 3D printed cartridge has been designed to house the sensing paper and to be easily snapped into a dark box adapted for the detection with a smartphone.
This is the first orthogonal paper-biosensor for mercury (II) with two different detection methods providing a readout within 15 min for colorimetric and 60 min for bioluminescent detection with a limit of detection for Hg(II) at the ppb levels. The device was also used to detect mercury in environmental samples, supporting its feasibility as a rapid and sensitive screening tool.

pH Colorimetric sensor Arrays based on acid-base indicators enhanced by surfactants

Andrea Pastore, Denis Badocco, Paolo Pastore [a]

[a] University of Padua, Department of Chemical Sciences, Via Francesco Marzolo 1, 35131, Padova (Pd).

The interest in the field of Colorimetric Sensor Arrays (CSAs) is growing owing to their easy construction and the detection system based on color variations measured with CCD cameras or scanners. In particular, pH CSAs have drawn much attention since they potentially do not suffer from drawbacks typical of glass electrode measurements such as slow response time, alkaline, and acidic errors, and variation of the liquid junction potential. The old pH CSAs proposed so far suffered from at least one of these issues: leaching at pH > 9, slow time response (especially at low temperatures), short shelf-life, large prediction errors (≥ 0.10 pH units), and limited working interval. We developed pH CSAs based on a single pH indicator embedded in an *OrMoSil* matrix able to detect pH values in large pH intervals by modulating its p*K*a value with the addition of suitable surfactants. The hexadecyltrimethylammonium p-toluenesulfonate demonstrated great potentialities for the sensor improvement in terms of reversibility, the fast response time (t_{95}< 30 s) and, repeatability together with prediction errors comparable to those of the glass electrode (≈ 0.01 pH units) [1-5]. The figure below represents the sensor components. From the pictures taken with a camera, the Hue coordinate from the HSV color space (Hue, Saturation, Value) is determined and related to the pH value. The Hue profiles vs. pH are constant and stable in time allowing a single calibration for sensors of the same lot. Each of the 45 sensing spots reported in the picture is characterized by its composition and therefore develops different colors for the same pH. The overall information reduces the pH error.



[1] A. Pastore, D. Badocco, L. Cappellin, P. Pastore, Microchem. J. (**2019**) 104552.
[2] A. Pastore, D. Badocco, P. Pastore, Talanta. 212 (**2020**), 120739.
[3] A. Pastore, D. Badocco, P. Pastore, Talanta. 219 (**2020**), 121251.
[4] A. Pastore, D. Badocco, P. Pastore, Talanta, 213 (**2020**) 120840.
[5] A. Pastore, D. Badocco, P. Pastore, Microchem. J. 157 (**2020**) 104891.

Application of whole-cell analytical bioassay based on turn-on chemiluminescence dioxetane probe sensing to quantify intracellular H_2O_2 in nutraceutical and biomedical fields

Angela Punzo [a], *Alessia Silla* [b], *Domenica Tonelli* [c], *Patrizia Simoni* [d], *Cristiana Caliceti* [b,e] *and Aldo Roda* [a,e].

[a]*Dept. of Chemistry "Giacomo Ciamician",* [b]*Dept. of Biomedical and Neuromotor Sciences-DIBINEM,* [c]*Dept. of Industrial Chemistry "Toso Montanari",* [d]*Dept. of Medical and Surgical Sciences – DIMEC,* [e]*INBB, National Institute of Biostructures and Biosystems.*

Hydrogen peroxide (H_2O_2) is an unavoidable by-product of cell metabolism and when it is not properly managed by the body or is produced in excess it can lead to chronic pathologies. A rapid and simple all-in-one effect-based chemiluminescent bioassay for the selective detection of intracellular H_2O_2 in human living cells was developed. The bioassay relies on an adamantylidene - 1,2 - dioxetane probe containing an arylboronate moiety that in the presence of H_2O_2 is converted to the correspondent phenol, responsible for its selectivity[1]. The extreme simplicity of the method, its high selectivity, low detection limit (0.15 µM), and ability to cross cell membrane (LogP = 5.46) make the probe suitable to be employed for the quantification of intracellular H_2O_2 in different living human cells type exposed to different pro-oxidant stimuli (i.e., menadione, PMA and LPS)[2]. As a proof of concept, the bioassay has been used to measure the antioxidant activity of three red pomace extracts highly enriched in malvidin, obtained from a "green" extraction process with natural deep eutectic solvents - NaDES (betaine: citric acid, betaine: urea, betaine: ethylen glycol) on 3D human keratinocytes. Under optimized conditions, 24 h treatment of betaine: citric acid formulation significantly decreased the intracellular H2O2 production in human 3D keratinocytes, obtaining an IC50 of 1.8 µg/mL in malvidin content. Moreover, the probe was employed to monitor the intracellular H_2O_2 production in peripheral blood mononuclear cells (PBMCs) from hypercholesterolemic subjects (n=15) before and after 2-month treatment with Evolocumab, a new generation LDL-cholesterol lowering drug [3]. Results clearly showed a significant decrease in H_2O_2 production by PBMCs ($p<0.007$) and this was associated to an improvement of arterial stiffness measured by carotid femoral Pulse Wave Velocity ($p<0.044$) and a decrease in Heme Oxygenase- 1 expression ($p<0.0047$). These data support the view of using Evolocumab to reduce cardiovascular disease risk independently of its serum LDL level lowering activity.

[1] O. Green, T. Eilon, N. Hananya, S. Gutkin, C.R. Bauer & D. Shabat, *ACS Cent. Sci.* **2017**, *3*, 349-358.
[2] D. Calabria, M. Guardigli, M. Mirasoli, A. Punzo, E. Porru, M. Zangheri, ... & A. Roda, *Anal. Biochem*. **2020**, *600*, 113760.
[3] M. Bove, A.F. Cicero & C. Borghi, *Expert Opin Emerg Drugs*, **2019**, *24*, 63-69.

Non-natural antibody-protein communication mediated by a synthetic DNA responsive device

Simona Ranallo,[a,b] Daniela Sorrentino,[a] Gianfranco Ercolani,[a] Kevin W. Plaxco,[b] Francesco Ricci [a]

[a] Department of Chemical Science and Technologies, University of Rome, 00133, Italy; [b] Department of Chemistry and Biochemistry, University of California Santa Barbara, CA93106, United States.

Dynamic interactions between DNA, RNA and proteins play a major role in the functioning of living systems.[1] These communication processes rely on highly complex networks with specific regulative functions. A "two-way" in-vitro DNA/protein communication can be achieved by exploiting the chemical versatility of synthetic DNA-based systems as versatile translator devices.[2] Such interface of two otherwise non-communicating proteins would represent an important step towards the applicability of these systems in more complex clinical settings. Motivated by the above considerations, we have developed an antibody-responsive DNA-based device that can mediate non-natural antibody-protein communication (Figure 1). To achieve this, we have employed a DNA-based device that comprises a synthetic DNA antibody-responsive unit (grey) conjugated at the two ends with a pair of antigens (blue hexagon). The antibody-responsive unit can recognize and sequester a specific single strand DNA (i.e. "translator", green) through the formation of a triplex structure. Such translator strand is designed to interact and inhibit a target protein and remain inactive when bound to the antibody-responsive unit. The antibody binding to the responsive unit triggers a conformational change that induces the release and activation of the DNA translator from the responsive unit thus allowing the communication between the target antibody and the selected protein.[3] We have characterized two antibody-responsive devices designed to respond to different target antibodies in an orthogonal way. Then, to demonstrate the possibility of using such DNA-based systems to enable artificial communication between non-naturally interfaced biomolecules, we have employed the above optimized antibody-responsive devices to achieve a downstream regulation of the activity of two different proteins. Specifically, we modulated the proteolytic activity of thrombin and the exonuclease activity of Taq DNA Polymerase. Recreate communication pathways where DNA, RNA and proteins interact with each other with programmed reaction patterns and create new biotechnology tools can find applications in sensing, drug-delivery, cell imaging and control of logic gates.

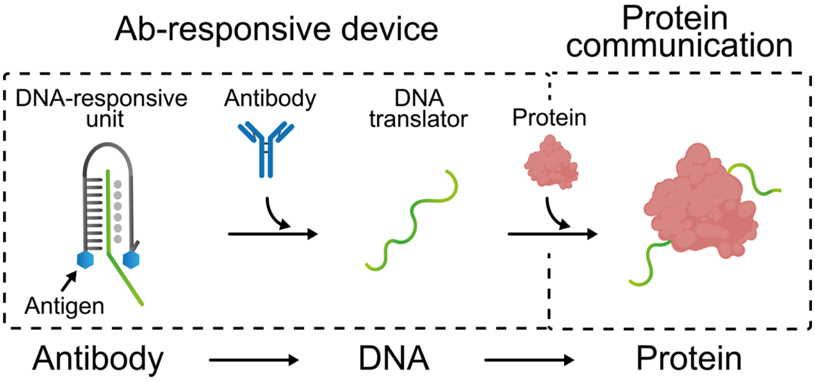


Figure 1. Antibody-protein communication controlled by an antibody responsive device. A DNA translator strand is released from a DNA responsive unit only in presence of a specific antibody thus allowing the downstream regulation of a protein.

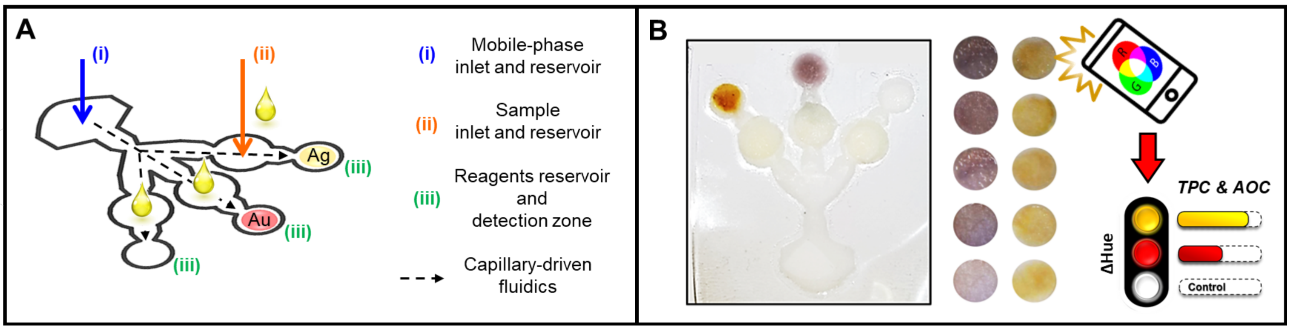
[1] E. E. Watson, S. Angerani, P. M. Sabale, N. Winssinger, *J. Am. Chem. Soc.* **2021**, *143*, 4467.
[2] R. Peri-Naor, T. Ilani, L. Motiei, D. Margulies, *J. Am. Chem. Soc.* **2015**, *137*, 9507.
[3] S. Ranallo, D. Sorrentino, G. Ercolani, K.W. Plaxco, F. Ricci, *(manuscript in preparation)*

Colorimetric paper-based analytical device for direct evaluation of olive oil phenols

Annalisa Scroccarello, Flavio Della Pelle, Dario Compagnone*

Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Campus "Aurelio Saliceti" via R. Balzarini 1, 64100 Teramo, Italy

The European Food Safety Authority claimed phenolic compounds (PCs) as functional molecules for health, recommending their daily intake [1]. Moreover, PCs are useful markers for food quality, able to bring added value to food [1]. The extra virgin olive oil (EVOO) is the main fat source of the Mediterranean diet and is a natural source of strong-antioxidant polyphenols[1, 2]. EVOO high lipids content hinders the direct and rapid analysis of total phenols content (TPC) and antioxidant capacity (AOC), which is conventionally performed after long and complex extraction procedures [1, 2]. Herein is presented a disposable and portable colorimetric lab-on-paper device able to assay simultaneously the TPC and AOC of EVOO, without the need for extraction. The proposed lab-on-paper is a pocket-sized device designed to enclose all the steps for the direct EVOO phenols evaluation as sampling, analyte transport, chemical reactions, and colorimetric detection. The lab-on-paper is fully composed of low-cost materials (chromatography paper, thermoplastic, and polymeric sheets), the device geometries were obtained with a craft-cutter machine, while the device assembling and nanoprobes formation were achieved by thermal lamination. In **Fig.A** is reported the sketch of the lab-on-paper, where is possible to observe the *inlets*, the *reservoirs*, and the *detection zones* for the housing of the colorimetric nanoprobes, compose of silver and gold nanoparticles. The lab-on-paper-based colorimetric assay relies on three steps (analysis time < 15 min): (*i*) sample loading, (*ii*) analytes transport to the analysis spot, and (*iii*) double colorimetric analysis exploiting the AuNPs and AgNPs growth on paper mediated by EVOO PCs. The colorimetric readout is easily acquirable throughout any digital camera. In **Fig.B** is possible to appreciate a photo of the device after analysis of olive oil with medium phenols contents. The Au and Ag-based colorimetric assays were calibrated employing hydroxytyrosol as the reference standard, achieving good linearity ($R^2 \geq 0.998$) and useful LODs (≤ 6 mg L^{-1}). The developed pocket device allowed the direct analysis of 30 EVOO samples, the data obtained resulted well correlate with conventional spectrophotometric methods ($r > 0.92$) for TPC (Folin-Ciocalteu) and AOC (ABTS) evaluation. The lab-on-paper result cost-effective (0.03 € per device) and exploitable out of labs. The here proposed devices pave the way for a new generation of everyone's reach customizable sensors, realizable with desk technology, and able to exploit nanomaterials unique features.



[1] D. Calabria, M. Mirasoli, M. Guardigli, P. Simoni, M. Zangheri, P. Severi, C. Caliceti, A. Roda, Sensors Actuators, B Chem. **2020**, 305

[2] F. Della Pelle, M. Sergi, M. Del Carlo, D. Compagnone, A. Escarpa, Anal. Chem. **2015**, 87, 6905–6911.

A competitive microplate bioassay to detect gonadorelin in urine samples *via* a polynorepinephrine-based molecular imprinted polymer

Francesca Torrini[a], Pasquale Palladino[a], Laura Caponi[b], Francesca Cipolli[b], Aldo Paolicchi[b], Simona Scarano[a] and Maria Minunni[a]

[a] Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy; [b] Laboratory of Clinical Pathology, University Hospital of Pisa, Via Roma 67, 56126 Pisa, Italy

Molecularly imprinted polymers (MIPs), named "plastic antibodies", are synthetic affinity reagents with tailor-made binding sites mimicking the ability of natural receptors to bind a target molecule. The latest decade has witnessed a great advance in MIPs and nowadays soft and biocompatible polymers, e.g. polydopamine (PDA) [1] and polynorepinephrine (PNE) [2], represent a powerful tool to detect bio-molecules such as proteins, peptides, glycoproteins, etc. Facile one-step synthesis, low cost, stability and reusability are some features that make them very attractive. Dopamine and norepinephrine are capable of self-polymerize in alkaline conditions leading to make adhesive nanolayers onto different surfaces. We recently started to investigate the potential application of PNE, in the biosensing field, which displays a markedly more hydrophilic and smoother surface compared to PDA. In particular, our study aimed to design a sensitive PNE-based assay to target a small peptide hormone of anti-doping interest, gonadorelin (MW = 1182.33 Da), which is improperly used by male athletes to improve their sports performances by stimulating the endogenous secretion of testosterone in the bloodstream. For this reason, gonadorelin (G) was banned by the World Anti-Doping Agency (WADA) and its detection represents a new frontier in antidoping research.

Here we report the development of a simple colorimetric microwell plate assay for sensitive gonadorelin detection based on MIP recognition, in line with our recent study performed with a benchtop SPR sensing platform [3]. In particular, a two-step competitive assay for G was designed by exploiting the competition between G and a signal-enhancer competitor molecule, biotinylated gonadorelin (BG) tethered to streptavidin-horseradish peroxidase (S-HRP).

The selectivity of the MIP towards gonadorelin recognition was addressed by testing another doping peptide i.e., leuprolide, and random peptides, all with comparable molecular weight. Some key parameters affecting assay performance such as template concentration for MIP synthesis, competitor molecule (BG) and enzyme (S-HRP) concentration, time and temperature of incubation and buffers composition were explored to find the best conditions for the successful of the competitive assay. Our findings corroborate the effectiveness of the imprinting strategy adopted in synthesizing MIPs for a small peptide hormone which are able to discriminate among peptides differing for only one amino acid. Urine artificial samples spiked with gonadorelin (0.006-16.9 μmol L^{-1}) were examined achieving a detection limit in the low ppb range with good reproducibility (%CV_{av} = 4.09), perfectly in line with the minimum required performance level (MRPL = 2 ppb) at which all WADA-accredited laboratories must operate in routine daily operations. The assay represents an interesting alternative tool to immunoassays with application to antidoping control. Besides, ongoing experiments are focused on directly testing urine samples with the designed bioassay in parallel with a reference analytical technique (HPLC-MS/MS) for assay validation.

[1] P. Palladino, M. Minunni, S. Scarano, *Biosens. Bioelectron.* **2018**, 106, 93–98.

[2] V. Baldoneschi, P. Palladino, M. Banchini, M. Minunni, *Biosens. Bioelectron*. **2020**, 1, 112161.

[3] F. Torrini, P. Palladino, V. Baldoneschi, S. Scarano, M. Minunni, *Anal. Chim. Acta* **2021**, 1161, 338481.

[4] F. Torrini, S. Scarano, P. Palladino, M. Minunni, *Anal. Bioanal. Chem*. **2021**, 413, 2217-2224

A spatial perspective to retrieve spatial-spectral signatures from overlapped components in spectroscopic imaging data

Mohamad Ahmad[a,b], *Raffaele Vitale*[b], *Cyril Ruckebusch*[b], *Marina Cocchi*[a]

[a]*Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, 41125 Modena, Italia*
[b]*Université de Lille, CNRS, LASIRE, F-59000 Lille, France*

A new paradigm has settled within various science fields and in industry, with spectral imaging. This has not come to a surprise, due to the potential the technique has, mapping simultaneously spatial and spectral information. Specifically in near-infrared (NIR) spectral imaging, due to its non-destructive analyses and broad range of application in e.g., agriculture, forensics, and quality control. However, despite its recognition in the many fields and applications, some challenges must be tackled to fully uncover and exploit the spatial and spectral domains within the data. Specifically for highly diffusive and scattering samples, where the complex spatial composition is highly correlated to the spectral signature of the different components. We propose a novel framework to spectral image analysis, considering a spatial perspective, while still retaining the information within the spectral domain. The framework utilizes firstly, wavelet transform (WT) decomposition to highlight distinct spatial features, within the NIR spectral image. Secondly, image coding with a set of descriptors, to reduce the dimensionality and describe the significant spatial features within the decomposed dataset. Thirdly, multivariate data analysis, to isolate the significant spatial-spectral information that is highlighted with the descriptors. Lastly, modelling, to use the extracted spatial-spectral information on newly acquired datasets. A forensic case study is used as a benchmark, with completely overlapping spatial components and highly overlapping spectral signatures. The first spectral image is of a piece of white cotton fabric that is stained with semen (mean image, *fig. 1a*), while the second dataset is a piece of red cotton fabric stained with semen (originated from the same donor; mean image, *fig. 1c*). The two data have noticeably different scattering effects, coming from the rough surface of the cotton fabric, with slightly different spectral signatures (due to the coloring of the fabric). The shape and intensity of the semen stain is different as well, as the semen is not observed in the mean image of the white cotton fabric. The results (*fig. 1c/d*) are promising as, the model shows different isolated spatial-spectral components, and it is simultaneously capable to isolate similar components from noticeably different data.

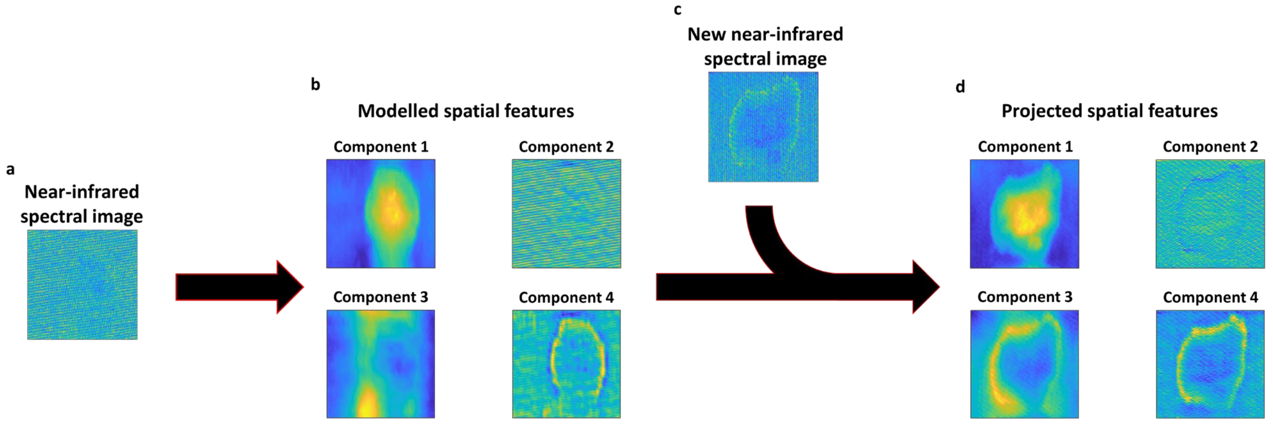


Figure 1: Framework of methodology. a) mean image of semen-stained white cotton fabric; b) results of the method, isolated spatial features from the spectral image; c) mean of semen-stained red cotton fabric; d) results of the projection of (c) onto model (b).

[1] M. Ahmad, R. Vitale, C.S. Silva, C. Ruckebusch, M. Cocchi, Exploring local spatial features in hyperspectral images, Journal of Chemometrics 34 (2020). https://doi.org/10.1002/cem.3295.

Quantification of rind percentage in grated Parmigiano Reggiano cheese by NIR-hyperspectral imaging and evaluation of the effect of factors related to sample preparation and composition

R. Calvini[a,b], S. Michelini[c], V. Pizzamiglio[c], G. Foca[a,b], A. Ulrici[a,b]

[a] *Department of Life Sciences, University of Modena and Reggio Emilia, Pad. Besta Via Amendola, 2, Reggio Emilia, 42122, Italy;*
[b] *Consorzio INSTM, 50121 Firenze, Via G. Giusti 9, Italy;*
[c] *Parmigiano Reggiano Cheese Consortium, Via J.F. Kennedy, 18, Reggio Emilia, 42121, Italy*

Rind percentage in grated Parmigiano Reggiano (P-R) cheese products is one of the quality parameters ruled by the Specifications of Parmigiano Reggiano cheese: this value should not exceed the limit of 18% (w/w).

In this study, funded by Parmigiano Reggiano Consortium, we evaluated the potential of Near Infrared Hyperspectral Imaging (NIR-HSI) for the determination of rind percentage in grated P-R cheese. Indeed, thanks to the possibility of acquiring both spatial and spectral information from a sample, NIR-HSI is an effective technique to analyse inhomogeneous food matrices, like grated cheese, with limited sample preparation and short times of analysis [1].

In a preliminary step, we acquired grated cheese samples with increasing levels of rind percentage ranging from 0% to 40% using a line-scanning NIR-HSI system working in the 1000-1650 nm spectral range. The hyperspectral images were converted into Common Space Hyperspectrograms (CSH), one-dimensional signals obtained by merging in sequence the frequency distribution curves of quantities calculated from a Principal Component Analysis (PCA) model common to the whole dataset of images [2]. The matrix of CSH signals was used to develop a calibration model using Partial Least Squares (PLS) algorithm to predict rind percentage, obtaining satisfactory results [3].

However, in order to extend the proposed approach to a practical application it is necessary to consider also the influence of the main variability sources involved in the preparation of P-R grated cheese, such as fat content of the pulp and grater type.

To this aim, grated cheese samples were prepared according to a full factorial experimental design considering three levels of rind percentage (8%, 18% and 28%), two levels of fat content of the pulp and two grater types (drum grater and knife mill). The corresponding hyperspectral images were converted into average spectra and CSH signals, and the resulting datasets were analysed using Analysis of Variance Simultaneous Component Analysis (ASCA) [4] in order to assess the effect of the considered factors.

[1] A.A. Gowen, C.P. O'Donnel, P.J. Cullen, G. Downey, J.M. Frias, *Trends Food Sci. Technol.* **2007**, 18(12), 590.
[2] R. Calvini, G. Foca, A. Ulrici, *Anal. Bioanal. Chem*. **2016**, 408(26), 7351-7366.
[3] R. Calvini, S. Michelini, V. Pizzamiglio, G. Foca, A. Ulrici, *Food Control* **2020**, 112, 107111.
[4] A.K. Smilde, J.J. Jansen, H.C. Hoefsloot, R.J.A. Lamers, J. Van Der Greef, M.E. Timmerman, *Bioinformatics* **2005**, 21(13), 3043.

Multivariate online monitoring of a powder blending process using a miniaturized near infrared sensor

Cristina Malegori [a], *Paolo Oliveri* [a], *Vanina Borghi* [b], *Diana Carolina Angel* [b], *Paola Melli* [b], *Eleonora Mustorgi* [a], *Monica Casale* [a].

[a] *DIFAR - Department of Pharmacy, University of Genova, Viale Cembrano 4, 16148 - Genova*
[b] *Medi Nova s.a.s., Via Beethoven 2/A - 42122 Reggio Emilia*

Semen extenders (SE) are zootechnical products added to animal semen as diluent and preservative before artificial insemination procedures. In the present work, the blending process of a commercial boar semen extender is monitored by means of a miniaturized near infrared (NIR) device coupled with multivariate process monitoring. A key-step of SE production is the blending phase, in which all the ingredients are mixed together until the endpoint of the process is reached, so that the product can be considered as homogeneous as possible. The definition of the process endpoint is, usually, done according to a specific blending duration, decided on experience bases – an approach that is totally blind to any modification occurring during the process itself.

Aim of the present work is the development of a strategy for the monitoring of the blending phase in a continuous and non-destructive way, determining a specific process endpoint for every single batch, in a quality by design (QbD) view.

In order to reach the aim, a MicroNIR PAT-U sensor (Viavi Solutions), working in the spectral range between 900 and 1700 nm, was directly clamped on the blender, enabling the acquisition of a spectrum every 4 s, through a sapphire window during the whole process. It is important to remark that, before the implementation of the NIR sensor, the endpoint of SE blending was set at 20 min. Spectra were acquired for 20 batches of *SE*, used as calibration set, and the strategy was validated on other 6 independent batches.

On the collected signals, a proper data pretreatment was performed by means of standard normal variate (SNV) transform combined with Savitzky–Golay first derivative (5 datapoint window, second polynomial order). Then, standard deviation spectra were calculated applying a moving-block strategy with a block size equal to 5 spectra. This step generates new profiles that summarize the informative spectral variation without being influenced by unwanted systematic variations between the batches, such as changes in particle size/humidity of the ingredients or variations of the environmental conditions. After a proper mean-centering, principal component analysis (PCA) was applied on the calibration batches, including only the spectra of the mixed products. Based upon knowledge and previous exploratory analyses, the product was considered mixed after 15 min of blending. The validation batches were, then, projected into the space defined by the two lowest-order principal components, accounting for more than 90% of the explained variance. The number of components was decided thanks to a dedicated cross-validation strategy. The influence plot (Hotelling's T^2 *vs*. Q residuals) and its statistical boundaries at a 95% confidence level were implemented as a multivariate control chart, for the monitoring of the behavior of new batches in the orthogonal space defined by PCA. The endpoint criterion was defined after acceptance of 15 consecutive spectra accepted by the multivariate control chart. Thanks to the present approach, the average time of the process was reduced to 5 min.

The whole strategy was implemented in a dedicated software, called *NIRNova*, developed in house with Matlab App Designer. Thanks to *NIRNova*, the production of *SE* is now monitored continuously in a non-destructive way, with a definition of the process endpoint for every single batch. Uniformity tests demonstrated that, despite the significantly time reduction, the final product is properly mixed. Moreover, an improvement of the product quality was highlighted, in terms of reduction of undesirable chalking and of temperature fluctuation of the powder.

A Paper-Based Electrochemical Device for the Detection of Pesticides Inspired by Nature: a Flower-Like Origami Biosensor

Veronica Caratelli[a], *Greta Fegatelli*[a], *Fabiana Arduini*[a,b], *Danila Moscone*[a]

[a]*Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica, 00133, Rome Italy*
[b]*Sense4Med, Via Renato Rascel 30, 00128, Rome Italy*

Pesticides are largely used at worldwide level to improve the food production, fulfilling the needs of the global population, which is increasing year by year. Although persistent pesticides (e.g. DDT) have been replaced with less persistent ones, contamination of food, soil and water by pesticides remains an issue of public concern. To better manage this problem, EU sets regulations for a sustainable employment of pesticides by promoting the adoption of Integrated Pest Management (Directive 2009/128/EC). In this overall scenario, the detection of pesticides in liquid and aerosol solutions at low concentrations (ppb level) is required to accomplish the regulatory aspect and to preserve the health of environment and human being. Herein, we propose a flower-like origami paper-based device for the detection of several classes of pesticides by combining different enzyme-inhibition biosensors. This device was developed by integrating two different office paper-based screen-printed electrodes and multiple filter paper-based pads to load enzymes and enzymatic substrates. The versatile analysis of different pesticides was carried out by folding and unfolding the filter paper-based structure, without any addition of reagents and any sample treatment (i.e. dilution, filtration, pH adjustment) [1]. The paper-based platform was employed to detect paraoxon, 2,4-dichlorophenoxyacetic acid and glyphosate at ppb level by exploiting the capability of these different types of pesticides to inhibit butyrylcholinesterase, alkaline phosphatase and peroxidase enzymes respectively. The degree of inhibition, correlated to the quantity of pesticides, was chronoamperometrically evaluated, monitoring the enzymatic activity in the absence and in the presence of pesticides by using a portable potentiostat. To improve the sensitivity, the paper-based electrodes were modified with carbon black nanoparticles in the case of platforms for 2,4-dichlorophenoxyacetic acid and glyphosate detection or carbon black decorated with Prussian blue nanoparticles for the detection of paraoxon. The detection of 2,4 D herbicide and paraoxon pesticide in gas phase was performed using a commercial portable nebuliser (SIMBR aerosol system) and the LOD obtained was 30 ppb and 2 ppb respectively (calculated as the amount of analyte which gives 10% of inhibition).

[1] F. Arduini, S. Cinti, V. Caratelli, L. Amendola, G. Palleschi, D. Moscone. *Biosens. Bioelectron.* **2019**, *126*, 346-354.

A multiparametric electrochemical device for degradation monitoring in reinforced concrete

Noemi Colozza [a], Sara Tazzioli [a], Alessandro Sassolini [b], Lorenzo Agosta [c], Maria Giuseppina di Monte [d], Kersti Hermansson [c], Fabiana Arduini [a,e]

[a] *University of Rome Tor Vergata, Via della ricerca scientifica, Roma, Italia*
[b] *ARPA Lazio, Via Salaria per L'Aquila 6-8, 02100 Rieti, Italy*
[c] *Department of Chemistry-Ångström, Uppsala University, Box 538, S-75121 Uppsala, Sweden*
[d] *Director of Museo Giacomo Manzù (Ardea), Direzione Regionale Musei Lazio, Piazza San Marco 49, 00186 Rome, Italy*
[e] *Sense4Med, Via Renato Rascel 30, Roma, Italia*

Reinforced concrete has become a leading material for the building sector in the 20th Century, thanks to the low costs and mechanical robustness that characterized this material. However, the occurrence of chemical processes that cause the degradation of reinforced concrete has drawn the attention to the need of monitoring the conditions of concrete-based structures over time. The primary concern is due to the corrosion of the reinforcement, which occurs when the passivating layer of iron oxides is degraded. Common environmental phenomena can promote the corrosion, for example pH alterations and chloride penetration [1].

In the present work, we designed a miniaturized potentiometric device for the fast and easy monitoring of reinforced concrete conditions. The presented device is composed by a screen-printed sensor combined with filter paper pad. The filter paper was designed with an envelope-like shape to be easily applied to the sensor as a disposable and smart material, in place of the materials commonly used to electrochemically interface the electrode with the solid surface of the concrete (e.g., wet sponge, electrolyte gels) [2]. The design of this device was conceived to allow for the multiparametric monitoring of the corrosion probability as well as for pH monitoring. The working principle is based on a three-electrode cell printed on the polyester support. By exploiting the same reference electrode, i.e. Ag/AgCl printed electrode, the measurement of corrosion probability or the pH of concrete can be obtained by a 30 s-long measurement. The former is achieved by measuring the electrochemical potential versus the metallic reinforcement as the working electrode; the latter is measured against the printed graphite working electrode, where an iridium oxide (IrOx) film is electrodeposited as pH-sensitive layer [3]. The resulting device was firstly tested on laboratory-prepared concrete samples upon different conditions, then the real-life applicability was proved by carrying out in-field measurements at the Giacomo Manzù museum, in Ardea (Italy). Thanks to the capability of providing information both on the corrosion conditions and the pH of concrete with a non-invasive approach, our sensor represent an innovative alternative for an extensive monitoring of concrete-based buildings and artworks.

[1] L. Bertolini, B. Elsener, P. Pedeferri, R.B. Polder, 1st ed., Wiley, **2003**.
[2] E. Cano, A. Crespo, D. Lafuente, B. Ramirez Barat, *Electrochem. Comm.* 41 **2014, 16–19.**
[3] S. Carroll, R.P. Baldwin, *Anal. Chem.* 82 **2010**, 878–885.

Acknowledgements to INNOCONCRETE “Innovative tools for conservation and monitoring of artworks in concrete by exploiting electrochemical paper-based sensors, functionalized nanomaterials, and modelling”, financed by Italian Ministry of Education, University and Research (MIUR) within the Executive Program on Scientific and Technological Cooperation between Italian Republic and Sweden, through Ministry of Foreign Affairs and International Cooperation and the Swedish Research Council (VR).

Electrosynthesised ion imprinted polymers in development of sensor for Cd(II) ions determination in water

Marco Costa[a], Sabrina Di Masi [a], Alvaro Garcia-Cruz[b], Sergey A. Piletsky[b], Cosimino Malitesta[a]*

[a] Laboratorio di Chimica Analitica, Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Via Monteroni, 73100, Lecce (Italia); [b] Department of Chemistry, University of Leicester, University Road, LE1 7RH, Leicester, (UK)

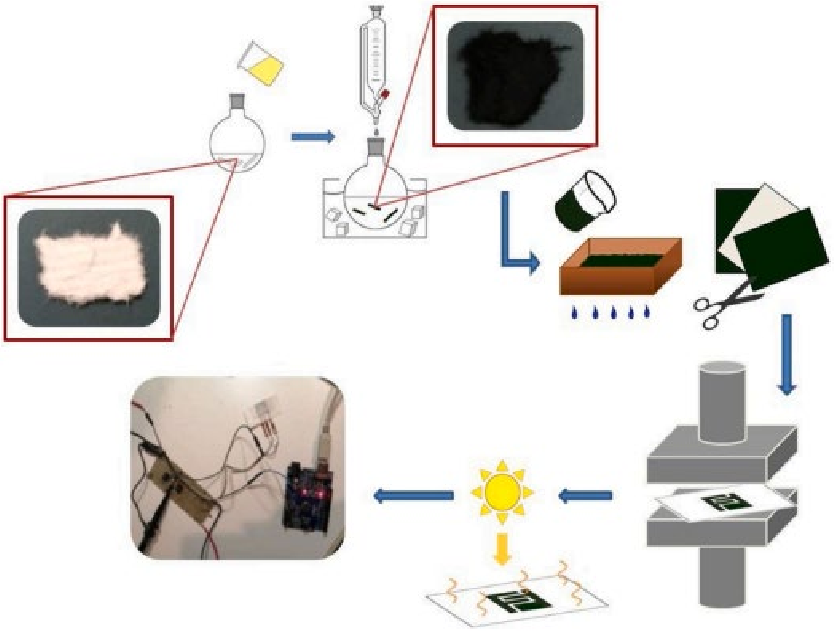
Imprinted polymers are artificial materials able to mimic recognition processes of antibodies, binding specifically analytes such as proteins, small molecules to ions. These polymers are promising materials for sensor development, as highly selective recognition elements. Superior properties of imprinted polymers generally rely on a recognition process involving imprinted cavities with complementary interactions between templates and functional groups. When ions act as template, an ion imprinted polymer (IIP) can be produced. Electrochemical synthesis of polymers is gaining increasing attention, mainly due to the advantage in producing imprinted polymeric film directly on the surface of electrodes during sensors development. Owing to that, we propose synthesis, characterisation, and application of a new electrosynthesised IIPs for the electrochemical detection of Cd^{2+} ions in water. Here, Cd^{2+}-IIP sensor was prepared by electropolymerisation of 4-aminophenylacetic acid (4-APA) monomer in the presence of Cd^{2+} ions (template). The screen-printed carbon electrodes (SPCE) were used as transducers, whereas the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were selected for electrochemical sensing of Cd^{2+} ions. The template removal was obtained by sensor incubation in NaOH 250 mM. FT-IR characterisation revealed differences between the polymer Cd^{2+}-IIP and its control (NIP film). SEM images were also recorded showing structural properties of synthesised films. The performances of sensors were observed in sodium acetate buffer over the Cd^{2+} concentration range 0.1 – 10 µM. An imprinting factor of 5 confirmed high specificity of Cd^{2+}-IIP. Selectivity studies of the Cd^{2+}-IIP were also carried out to assess the high selectivity of the imprinted cavities.

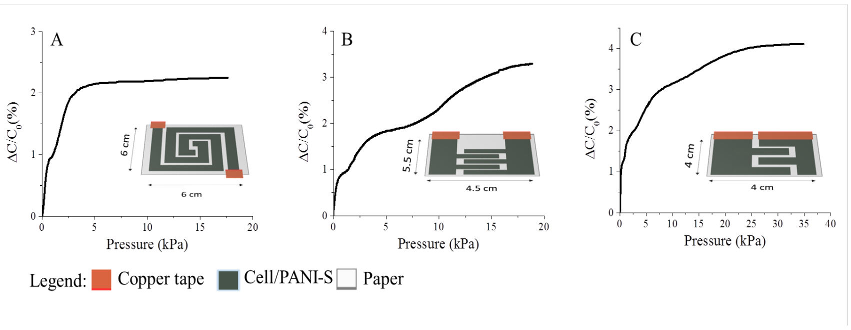
A simple and industrially scalable method for making a PANI-modified cellulose touch sensor.

*Ragazzini [a], I. Gualandi [a, *], S. Selli [b], C. Polizzi [a], M.C. Cassani [a], D. Nanni [a], F. Gambassi [a], F. Tarterini [a], D. Tonelli [a], E. Scavetta [a], B. Ballarin [a, *]*

[a] Department of Industrial Chemistry “Toso Montanari”, Bologna University, Viale Risorgimento 4, I-40136, Bologna, Italy; [b] Cromatos s.r.l., via G. Cardano, 6B/C/D, 47122, Forlì, Italy

Nowadays, alternatives to the traditional electronics that should be low cost, degradable, compostable and made from environmentally nontoxic substances are of great interest in research. As candidate, we propose bare fibers of cellulose made conductive by an in situ oxidative polymerization of aniline. The resulting composite fibers were emplojed to fabricate electroactive sheets using a pilot plant of a typical paper industry. The resistivity of the obtained sheets is 14 ± 1 Ω sq^{-1}, a value around 1000 times lower than those reported in literature. The higher electronic performances of the sheets were demonstrated by assembling a capacitive touch sensor device with optimized geometry. The touch sensor shows an increase of 3–4 % of the starting electric capacity after compression and a fast response time of 52 ms. To our knowledge this is the first time that a device is prepared in this way and therefore, the herein presented results can bring a significant improvement in the development of low-cost, green and high-tech electronic devices [1].





[1] Ragazzini, I. *et al.* A simple and industrially scalable method for making a PANI-modified cellulose touch sensor. *Carbohydr. Polym.* (2020) doi: 10.1016/j.carbpol.2020.117304.

CONTAMINARSI FA BENE ALLA RICERCA

Luigia Sabbatini

Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", V. Orabona, 4, 70126, Bari, Italy

La parola "contaminazione", che deriva dal latino contaminare, tangere, toccare, in ambito tecnico ha sempre avuto un'accezione negativa, come, per esempio, contaminazione delle prove, contaminazione radioattiva, delle falde acquifere, degli alimenti, …. e noi Chimici ben lo sappiamo.
Oggi, uscendo da questo ambito tecnico, ha invece un'accezione positiva, indicando la fusione di elementi di natura diversa, la mescolanza di linguaggi e saperi diversi. Ma sempre più viene associata al termine innovazione e si ritiene che siano strettamente legati in una sorta di processo continuo all'interno della società globale e globalizzata, processo capace di portare a rapide e profonde trasformazioni in tutti gli ambiti delle relazioni umane.
Un tempo l'interdisciplinarità era la norma, non l'eccezione. Uno stragrande numero di scienziati che hanno sinora contributo allo sviluppo del sapere e del nostro mondo possono essere definiti "contaminati ad alto tasso di innovazione" [1], come esempio ci basti citare Leonardo da Vinci, il "contaminato per eccellenza".
Gli Illuministi, in prospettiva di un sapere che si stava ampliando sempre più, decisero di definire dei perimetri tra le discipline. Ed è proprio la prima rivoluzione industriale che catalizza questo processo perché ha bisogno, per far funzionare le nuove macchine, di nuovi professionisti specializzati.
Nell'Ottocento, poi, la specializzazione viene istituzionalizzata e le discipline si identificano con dipartimenti accademici universitari.
Ma i contaminati continuano a esistere e, nella ricerca, ci si rende sempre più conto che senza l'interdisciplinarità non si va da nessuna parte. In realtà la contaminazione è qualcosa di più che interdisciplinarità: è la fusione di ambiti culturali.
Senza nessuna pretesa di essere un esempio significativo, né, tantomeno, di paragonarmi alle eccellenti figure prima citate, in questa relazione presenterò le mie esperienze di contaminazione nello sviluppo temporale della mia attività di ricerca. Da studiosa delle "superfici" mi è capitato di dovermi "interfacciare" con ambiti disciplinari molto diversi da quello chimico. Certamente la contaminazione porta ad un arricchimento professionale e, nell'Università, dovrebbe investire sempre più anche il settore della formazione, come già avviene in interessanti realtà in diverse parti del mondo.

[1] Giulio Xhaet "Contaminati – Connessioni tra discipline, saperi e culture " – Hoepli Editore

Recent Developments in Mass spectrometry and Cutting Edge Scientific Innovation to Characterize Complex Samples

Luigi Mondello

Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy

A large panel of analytical methods based on separation techniques are commonly used to characterize complex samples. Most of them are based on chromatographic techniques hyphenated to Mass Spectrometry such as LC/MS, GC/MS and CE/MS. These methods are widespread and present some unique advantages. However, such approaches are characterized by long and complex sample preparation procedures, high cost per analysis, and time consuming assay protocols, so several working hours are required to get the final results. In the last decade, spectroscopic techniques such as nuclear magnetic resonance spectroscopy and near infrared spectroscopy have been successfully applied to achieve fast and accurate analyses. More recently, the exponential development of ambient mass spectrometry (MS) has opened a new scenario. The coupling of an ambient sampling device to powerful mass spectrometers, has demonstrated the potential to afford comprehensive molecular profiling to be used for identification/quantification and/or as a fingerprint (as an alternative to the proteome or lipidome).

The aim of the present lecture is to discuss the applicability and the advantages of direct mass spectrometry approaches, which vaporize and ionize molecules directly from the sample without any sample pre-treatment, and critically compare their robustness and accuracy with the more consolidated traditional approaches.

Is There a Real Need for Multidimensional Chromatography Strategies with the Current Availability of Powerful Mass Spectrometry Platforms?

Mariosimone Zoccali[a], *Peter Q. Tranchida*[b], *Luigi Mondello*[b,c,d,e]

[a] *Department of Mathematical and Computer Science, Physical Sciences and Earth Sciences, University of Messina, Messina, Italy;*
[b] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[c] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[d] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[e] *Department of Sciences and Technologies for Human and Environment, University Campus Bio-Medico of Rome, Rome, Italy*

Whether a sample is a solid, a liquid, or a gas, there are at least two levels of complexity that need to be taken into consideration when performing any chromatographic analysis. The first level of complexity involves the extraction of the analytes of interest from the sample matrix. However, even when proper sample preparation has been performed, there are several factors that contribute to the second level of complexity such as: the number of analytes, boiling point range, dynamic range in terms of concentration, and the presence of interferents. As a consequence, separations can be characterized by a number of coelutions due to the fact that there are either too many compounds to separate, too much of a difference in concentrations between analytes, or too many interferences. When the limited resolution of one-dimensional separation methods leads to excessive solute overlap, an obvious solution is to use a multidimensional chromatography system.

With regards to the use of mass spectrometry (MS), it is mandatory for the purpose of identification; apart from general qualitative profiling, MS can perform selective forms of detection, enabling the quantification of trace-amount analytes. Thus, mass spectrometry can be used for both untargeted and targeted analysis. The hyphenation a multidimensional chromatography technique and MS provides a powerful 3D technology, sometimes considered excessive, due to the evolution in the MS field in recent years.

The purpose of this lecture is to try to demonstrate the importance and advantages of such couplings that are sometimes considered wasteful, using multidimensional chromatography not only to enhance the separation power but also for sample preparation, obtaining an all-in-one automated system.

Boosting the downstream processing of biopharmaceuticals by means of multicolumn continuous chromatography

Martina Catani[a,*], *Chiara De Luca*[a], *Simona Felletti*[a], *Giulio Lievore*[a], *Alessandro Buratti*[a], *Desiree Bozza*[a], *Massimo Morbidelli*[b], *Alberto Cavazzini*[a]

[a]*Dept. Of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, via L. Borsari 46, 44121, Ferrara, Italy*
[b]*Dept. of Chemistry, Materials and Chemical Engineering Giulio Natta, Politecnico di Milano, via Mancinelli 7, 20131 Milan, Italy*
[*] *e-mail: martina.catani@unife.it*

Biopharmaceuticals have increasingly gained popularity in the last two decades. Thanks to their unique properties, including high affinity to specific target molecules or receptors and reduced side-effects in comparison to small-molecule drugs, this class of biomolecules has been used in the clinical treatment of many diseases, including cancer and metabolic disorders [1].

The industrial production (upstream processing) of biopharmaceuticals has tremendously advanced, especially for what regards cell culture and fermentation processes or solid-phase synthesis. However, these advancements have not been matched by equivalent improvements in purification procedures (downstream processing) which still represents the bottleneck, in terms of both cost and time, in the entire production process.

Industrial purification of biopharmaceuticals is usually carried out through single-column preparative liquid chromatography and more chromatographic steps are often required. The first one (capture step) makes use of affinity columns to remove all non-product-related impurities (such as host cells or DNA). Afterwards, one or more polishing steps are needed to isolate the target compound from product-related impurities (such as truncated species or diastereoisomers) [2].

However, single-column processes suffer of some intrinsic limitations. Indeed, in the capture step, the trade-off between capacity utilization and productivity can be very relevant, while polishing processes are characterized by yield-purity trade-off.

These limitations can be alleviated through multicolumn countercurrent continuous (or semi-continuous) chromatographic techniques. The employment of two or more identical columns, working either in parallel or interconnected, allows for the internal recycle of the product into the system. The greatest advantage of this approach is that the purification process can be completely automated, with minimum need of human intervention and considerable saving of time. Meantime, the reproducibility of the process is improved.

This communication will show the great potential innovative multicolumn platforms for the capture and the polishing steps in the manufacturing of biopharmaceuticals, with particular emphasis to Multicolumn Countercurrent Solvent Gradient Purification (MCSGP) for the polishing step. Different case studies will be discussed to show how these approaches can be applied to improve the purification of biopharmaceuticals, including monoclonal antibodies, peptides, and proteins [2,3,4].

[1] M. Kesik-Brodacka, *Biotechnol. Appl. Chem.* **2018**, *65*, 306-322
[2] C. De Luca, S. Felletti, G. Lievore, A. Buratti, M. Sponchioni, A. Cavazzini, M. Catani, M. Macis, A. Ricci, W. Cabri, *LCGC* **June 2020**, *Advances in HPLC systems technology*, 2-7
[3] M. Angarita, T. Müller-Späth, D. Baur, R. Lievrouw, G. Lissens, M. Morbidelli, *J. Chromatogr. A* **2015**, *1389*, 85-95.
[4] C. De Luca, S. Felletti, G. Lievore, T. Chenet, M. Morbidelli, M. Sponchioni, A. Cavazzini, M. Catani, *TrAC* **2020**, *132*, 116051

Release of selected non-intentionally added substances (NIAS) from PET food contact materials: a new and validated SPE online-UHPLC-MS/MS multiresidual method

Riccardo Aigotti[a], Nicola Giannone[a], Enrica Mecarelli[a], Federica Dal Bello[a], Alberto Asteggiano[a], Claudio Medana[a].

[a] *Dipartimento di Biotecnologie Molecolari e Scienze per la Salute, University of Turin*

FCMs (Food Contact Materials) are an underestimated source of food chemical contaminants and a potentially relevant route of human exposure to chemicals harmful to endocrine system; this exposure occurs much by foods and water, which came in contact with polymeric nature packaging.

Reg. (EU) 10/2011 requires migration tests on food contact materials and foodstuffs to evaluate the presence of positive listed substances (authorized monomers and additives) and much more not intentionally added substances (NIAS) not listed in the regulation and do not subject to restrictions. All of this to ensure compliance for food contact.

The development and validation of this online SPE /UHPLC-MS/MS method derives from the need to automate the analysis process, as much as possible, up to increase instrumental sensitivity to trace levels of unregulated substances.

Thanks to this method it was possible to detect trace levels of NIAS (ng/L) from PET foodstuff.

[1] M. Cherif Lahimer, N. Ayed, J. Horriche, and S. Belgaied, “Characterization of plastic packaging additives: Food contact, stability and toxicity,” Arab. J. Chem., vol. 10, pp. S1938–S1954, 2017, doi: 10.1016/j.arabjc.2013.07.022.

[2] P. Schmid and F. Welle, “Chemical migration from beverage packaging materials—a review,” Beverages, vol. 6, no. 2, pp. 1–19, 2020, doi: 10.3390/beverages6020037.

[3] P. Vera, E. Canellas, and C. Nerín, “Identification of non volatile migrant compounds and NIAS in polypropylene films used as food packaging characterized by UPLC-MS/QTOF,” Talanta, vol. 188, no. June, pp. 750–762, 2018, doi: 10.1016/j.talanta.2018.06.022.

[4] C. Bach, X. Dauchy, I. Severin, J. F. Munoz, S. Etienne, and M. C. Chagnon, “Effect of temperature on the release of intentionally and non-intentionally added substances from polyethylene terephthalate (PET) bottles into water: Chemical analysis and potential toxicity,” *Food Chem.*, vol. 139, no. 1–4, pp. 672–680, 2013, doi: 10.1016/j.foodchem.2013.01.046.

[5] European Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32011R0010&from=it

Characterization of Triacylglycerols in Hemp Derived Products by means of Ultra-High Performance Liquid Chromatography Coupled to Mass Spectrometry Detection

Paola Arena [a], *Francesca Rigano* [a], *Paola Dugo* [a,b], *Luigi Mondello* [a,b,c]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[c] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

Cannabis sativa is considered a multipurpose, low environmental impact crop and the term “hemp” generally refers to cultivars grown for industrial purposes. This species has great potential and economic value for the high quality of raw materials and the impressive seed oil content; in fact, hemp derived products are rich in omega-3 and omega-6 polyunsaturated fatty acids (PUFA), including especially alpha and gamma linolenic acids, linoleic acid, vitamins (particularly tocopherols), antioxidant molecules and minerals, such as potassium, magnesium and calcium.

The presence of high biological value molecules has determined a growing interest in the study of this species for the potential daily use as supplements, able to contribute positively to the regulation of the metabolic activities of the organism and the prevention of cardiovascular diseases.

In this research, hemp oil, meal and inflorescences were examined, predominantly focusing on the lipid fraction, with particular emphasis on triacylglycerols (TAGs) containing PUFA.

As it is well known, the reversed phase liquid chromatography (RP-LC) is the most suitable separation mechanism for the analysis of complex lipids; in fact, hydrophobic interactions between the target analytes and the stationary phase provide a separation of the mixture directly dependent on the partition number, calculated from the equation $ECN = CN - 2DB$ (equivalent carbon number, carbon chain length and double bonds number respectively).

For the investigation of lipid species, a linear retention index (LRI) approach in liquid chromatography coupled to mass spectrometry detection has been employed; the reference homologue series used for the calculation of retention indices consisted of a mixture of odd carbon number TAGs (C9C9C9-C19C19C19) covering the full elution range of target analytes contained in the samples of interest.

The identification process was based on a dual filter approach, specifically concerning the information obtained from mass spectra and retention behaviour of analytes. For the latter purpose, LRI were calculated and the obtained values were compared to an LRI TAGs database previously built in the laboratory, considering a tolerance window of ± 15. For the identification of some triacylglycerols, it was possible to use the spectral library search, achieved by recording the mass spectra of commercial standards.

The characteristic TAG composition, particularly concerning the ω-6 and ω-3 PUFA, make hemp-derived products useful food ingredients for daily consumption and for the formulation of nutraceuticals.

Development of a new method to study small molecules produced by microbiota from colorectal adenoma

Elettra Barberis[1,2], Soni Joseph[3], Elia Amede[1,2], Michela Giulia Clavenna[3], Marta La Vecchia[3], Marika Sculco[3], Anna Aspesi[3], Pietro Occhipinti[4], Elisa Robotti[5], Renzo Boldorini[3], Emilio Marengo[5], Irma Dianzani[3], Marcello Manfredi[1,2]

1 Department of Translational Medicine, University of Piemonte Orientale, Novara, Italy.
2 Center for Translational Research on Autoimmune and Allergic Diseases, University of Piemonte Orientale, Novara, Italy.
3 Department of Health Sciences, University of Piemonte Orientale, Novara, Italy.
4 Department of Gastroenterology, 'Maggiore della Carità' Hospital, Novara, Italy.
5 Department of Sciences and Technological Innovation, University of Piemonte Orientale, Novara, Italy.

The intestinal microbiota is composed of a large number of different bacteria that produce a variety of metabolites [1]. Colorectal cancer, which typically develops from adenomatous polyps, is highly influenced by microbiota [2]. Since a variety of molecular changes may occur as these polyps transform from benign tumor to malignant carcinoma, the ability to study the microbiota-produced metabolites can lead to new discoveries about the development and progression of this cancer. However, to address the complexity of the microbiota-produced molecules, novel methods are needed. To this aim, in the present work, we developed a high-throughput metabolomics method to capture the metabolic complexity of the microbiota metabolome adherent to adenomatous polyps and adenocarcinoma. For the first time, the method enables the simultaneous quantification of almost 300 metabolites, while preserving the integrity of the original sample. The metabolomics approach was analytically validated and had excellent performances in terms of recovery, linearity, specificity, intra- and inter-day precision, limits of detection, and quantification. Furthermore, the clinical potential of the method was demonstrated in adenoma collected for a colorectal adenoma study.

[1] Lynch, S. V.; Pedersen, O. The Human Intestinal Microbiome in Health and Disease. *N. Engl. J. Med.* **2016**, 375, 2369-2379.

[2] Arnold, C. N.; Goel, A.; Blum, H. E.; Boland, C. R. Molecular Pathogenesis of Colorectal Cancer: Implications for Molecular Diagnosis. *Cancer.* **2005**, 104, 2035-2047.

Fundamental study of purification of target peptides from their epimers by liquid chromatography

Desiree Bozza[1*], Alessandro Buratti[1], Chiara De Luca[1], Simona Felletti[1], Giulio Lievore[1], Walter Cabri[2], Alessandra Tolomelli[2], Alexia Mattellone[2], Marco Macis[3], Antonio Ricci[3], Martina Catani[1], Alberto Cavazzini[1]

[1] Department of Chemical, Pharmaceutical and Agricoltural Sciences, University of Ferrara, Ferrara 44121, Italy

[2] Department of Chemistry “Giacomo Ciamician”, Alma Mater Studiorum, University of Bologna, Bologna 40126, Italy; Fresenius Kabi iPSUM Srl, I&D, Villadose (Rovigo) 45010, Italy

[3] Fresenius Kabi iPSUM Srl, I&D, Villadose (Rovigo) 45010, Italy

Biopharmaceuticals have emerged as an innovative class of therapeutics peptides and their use for these scopes has been growing rapidly. Result of their highly specific activity, a feature that cannot be achieved by traditional drugs, peptides are increasingly used for treatment of symptoms associated with many diseases. Techniques like e.g., solid-phase synthesis is used for the industrial synthesis of peptides and other biomolecules. This technique has an important disadvantage that is the production, in addition to the target peptide, of various impurities having very often a similar structure and molecular characteristics to the target product (e.g., epimers). Single-column (batch) preparative liquid chromatography (LC) is the most employed technique for purification of peptides [1-2]. Due to preparative (or nonlinear) LC large volumes of concentrated multicomponent feed are processed in a single run with the purpose of isolating finite amounts of pure compounds. The retention of analytes, under overload conditions, becomes not only concentration-dependent also becomes dependent on the amount of any component adsorbed by the concentrations of all species in solution (competitive systems) [1-2]. It is essential typify the main impurities that could be present in a mixture of raw peptides for the complete characterization of the product in regulatory environments.

Aim of this work is the purification procedure via preparative liquid chromatography that has been then optimized on the basis of the type of crude peptide mixture in order to obtain pure fractions of the target peptide and its epimers. In this study a pharmaceutically relevant polypeptide made of 10 aminoacids and all its epimers have been separately synthesized by solid phase synthesis. It was observed that retention on a hydrophobic adsorbent is strongly influenced by a change in the configuration of a single amino acid (D- or L-) leading to a wide range of retention times.

[1] C. De Luca, S.Felletti, D. Bozza, et al. *Process Intensification for the Purification of Peptidomimetics: The Case of Icatibant through Multicolumn Countercurrent Solvent Gradient Purification*, MCSGP Industrial & Engineering Chemistry Research Article ASAP, 2021

[2] C. De Luca, S. Felletti, G. Lievore et al., *Modern trends in downstream processing of biotherapeutics through continuous chromatography: The potential of Multicolumn Countercurrent Solvent Gradient Purification,* TrAC Trends in Analytical Chemistry, Vol. 132, 2020,116051.

Glucosinolate hydrolysis by myrosinase in *Brassicaceae* tissues: a chromatographic approach

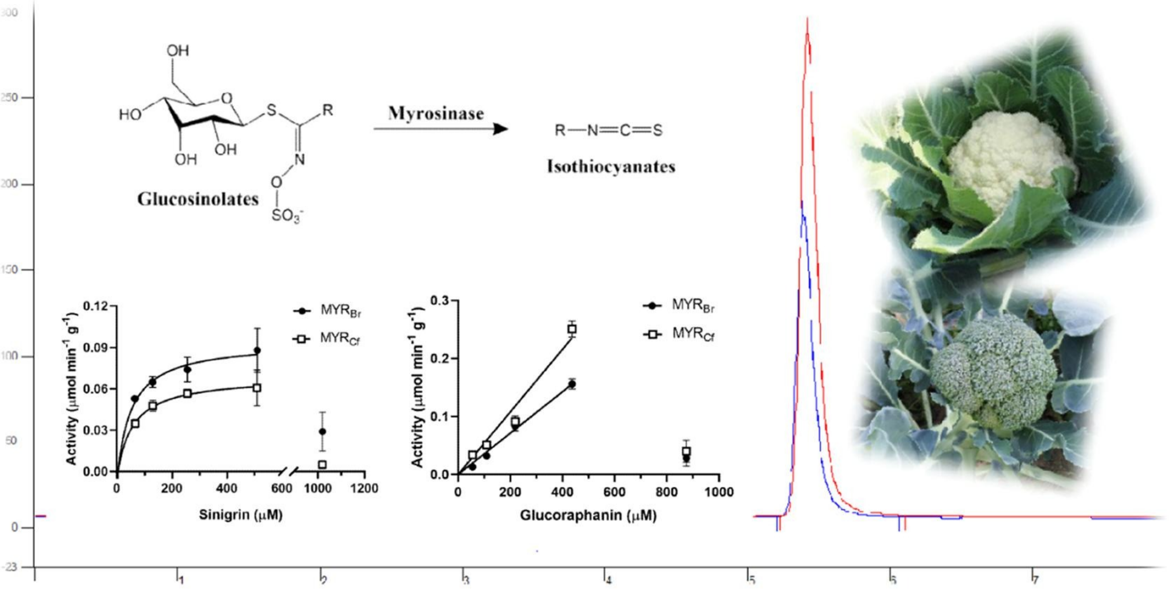
Marco Consumi[abc]*, *Gabriella Tamasi*[ab], *Claudia Bonechi*[ab], *Claudio Rossi*[ab]

[a]*Department of Biotechnology, Chemistry and Pharmacy (DBCF), University of Siena, via Aldo Moro 2, 53100 Siena, Italy*
[b]*Center for Colloid and Surface Science (CSGI), University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy*
[c]*National Interuniversity Consortium of Materials Science and Technology (INSTM), via Giuseppe Giusti 9, 50121 Florence, Italy*

Glucosinolates are a group of secondary metabolites occurring in all the vegetables belonging to the Brassicaceae family. Upon tissue damage, glucosinolates are hydrolysed by myrosinase to a series of degradation products, including isothiocyanates, which are important for their health-promoting effects in humans. The glucosinolate/myrosinase system has been characterized in several Brassica species, of which white mustard (Sinapis alba) has been studied the most.

Usually, the studies of glucosinolates hydrolysis involves their extraction by hot methanol, to inhibit their hydrolysis by the myrosinase. Then, the hydrolysis follow up is determined by UV spectroscopy assay.

In this study we develop a totally new approach both about the extraction of glucosinolates, we used a pH=2 phosphate buffer solution and HPLC-UV assay to evaluate the activities and kinetics of myrosinases in aqueous extracts, which closely represent the physiological conditions of plant tissues. This method was tested on myrosinases extracted from broccoli and cauliflower inflorescences, employing sinigrin and glucoraphanin as substrates. The results confirm the feasibility of the water-based extraction method as alternative to methanol extraction. In addition, the HPLC-UV assay proposed already shows its potential highlighting the strong inhibition of both enzymes at high substrate concentrations. The main issues related to kinetic analysis on the glucosinolate-myrosinase system were also elucidated.



High performance liquid chromatography coupled to mass spectrometry for the analysis of *H. sabdariffa* bioactive compounds in simulated human digestion model

Yassine Oulad El Majdoub[a],, Francesco Cacciola[b], Giuseppina Mandalari[a], Paola Dugo[a,c], Luigi Mondello[a,c,d,e]*

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*
[b] *Department of Biomedical, Dental, Morphological and Functional Imaging Sciences, University of Messina, Messina, Italy*
[c] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[d] *Department of Sciences and Technologies for Human and Environment, University Campus Bio-Medico of Rome, Rome, Italy.*
[e] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy.*

Abstract: *Hibiscus sabdariffa L.* (*H.s.*) is a plant rich in polyphenols commonly consumed as a beverage or spice. The aim of the present study was to evaluate the metabolism of the bioactive compounds after their *in vitro* digestion in a human digestion model which simulates the human stomach and duodenum. For polyphenol characterization, high performance liquid chromatography coupled to mass spectrometry detection, equipped with an electrospray ionization (ESI) source, was employed in both positive and negative ionization modes. Bioaccessible polyphenols in digestive aliquots were extracted and purified using a solid-phase extraction (SPE) technique. Anthocyanins of *H. sabdariffa* (Cyanidin-3-O-sambubioside and Delphinidin-3-O-sambubioside) content have drastically dropped throughout the digestion process from 2.88 ± 0.03 µg g-1 (*w/w*) and 8.51± 0.08 µg g-1 (*w/w*) CG (Cyanidin-glucoside) in the undigested extract to 0.10 ± 0.01 µg g-1 (*w/w*) and 0.09 ± 0.01 µg g-1 (*w/w*) CG at the end of duodenal digestion, respectively. On the other hand, the decrease in certain compounds (*e.g.* caffeoylquinic acids and coumaroylquinic acid) was observed in gastric digestion resulting in an increase of quinic acid in duodenal aliquots, suggesting how this compound was derived from the degradation of the more complexed hydroxycinnamic acid.

Comparing mixed-mode and hydrophobic stationary phases for the purification of a large therapeutic peptide

G. Lievore[1*], C. De Luca [1], S. Felletti [1], A. Buratti [1], D. Bozza [1], M. Macis [2], A. Ricci [2]

M. Catani [1], A. Cavazzini [1]

[1] University of Ferrara, via Luigi Borsari 46, Ferrara, Italy

[2] Fresenius Kabi iPSUM, via San Leonardo 23, Villadose, Italy

* Email: giulio.lievore@unife.it

In recent times, the purification of biopharmaceuticals has gained pharmaceutical production has been increasingly devoted to the manufacturing of highly sophisticated, complex and biological-derived molecules.

Their manufacture consists basically of two steps: the upstream where a biotechnological system or chemical synthesis is employed for the production of the target molecule, followed by the downstream processing needed to isolate the target [1] to meet quality specifications required by Regulatory Agencies.

Modern preparative liquid chromatography (LC) represents the most suitable technique for the purification of mixtures of large biomolecules [2].

In this work, different experimental conditions were compared for the chromatographic purification of a raw mixture of Liraglutide (a therapeutic peptide, made of 32 amino acids and structurally analogous of the endogenous GLP-1, applied in the treatment of hyperglycaemia [3]) produced through solid phase synthesis.

For the comparison study, four different columns of same dimensions (250 mm x 4.6 mm) packed with two different stationary phases (mixed-mode and C8) were tested under the same experimental conditions (mobile phases and gradient).

The experimental data have evidenced that mixed-mode columns allow to achieve more favourable mass transfer and adsorption thermodynamic compared to C8 ones. This is due to the presence of negatively charged groups on the surface of mixed-mode stationary phases inducing an electrostatic interaction in addition to hydrophobic ones.

On mixed mode stationary phases, better resolution and selectivity between target and product-related impurities was observed leading to the increase of target purity and process recovery and productivity.

[1] De Luca C., Felletti S., Lievore G., Morbidelli M., Sponchioni M., Cavazzini A., Catani M. *TrAC “Modern trends in downstream processing of biotherapeutics through continuous chromatography: The potential of Multicolumn Countercurrent Solvent Gradient Purification”* **2020,** *132*, 116-118.

[2] Karst, D.J., Steinebach, F., Morbidelli, M. *Curr. Op. in Biotech “Continuous integrated manufacturing of therapeutic proteins”* **2018**, *53*, 76-84.

[3] Vilsbøll T. *Drug Eval. “Liraglutide: a human GLP-1 analog for Type 2 diabetes”* ***2009,*** *6, 199–207.*

“Extractor Naviglio (RSLDE)” performs green extractions: evolution over time and new applications in the last two decades.

D. Naviglio[1], D. Montesano[2], M. Ciaravolo[1], A. Savastano[1], V. Nebbioso[1], M. Gallo[3]

[1]Department of Chemical Sciences, University of Naples Federico II, via Cintia, 4, 80126 Naples, Italy; [2]Department of Pharmacy, University of Naples Federico II, via D. Montesano 49, 80131 Naples, Italy; [3]Department of Molecular Medicine and Medical Biotechnology, University of Naples Federico II, via Pansini, 5, 80131 Naples, Italy.

Solid-liquid extraction procedures are at the basis of numerous production processess, such as the production of alcoholic and non-alcoholic beverages, enoliths, brutolites, oil flavoring, vegetable food supplements, mother tinctures, glycerine macerates, natural perfumes and aromas. Traditionally, solid-liquid extractions were performed using organic and/or inorganic liquids and their mixtures as extractant solvents in contact with an insoluble solid matrix (e.g., the Soxhlet method) or using atmospheric pressure static systems that require long times such as maceration or systems that lower in efficiency such as percolation. Nowadays, everything has changed with the introduction of tools that reduce extraction time and solvent consumption, improve extraction efficiency and decrease environmental impact (green extractions). All this is based on a new way of thinking about chemistry, the so-called green chemistry, based on the prevention of pollution which involves the development of systems that use and produce substances with a lower risk for human health and with a low environmental impact. Exploiting the principles of green chemistry means implementing a series of principles that reduce or eliminate the use and production of hazardous substances during all stages of processing. It is precisely in this wake of eco-sustainability and green chemistry that rapid solid-liquid dynamic extraction (Extractor Naviglio RSLDE) fits. The extraction takes place by generating a negative pressure gradient from the inside towards the outside of the solid matrix, so it can be conducted at room temperature or even sub-environment [1]. Literature data have shown the versatility of extractor Naviglio (RSLDE) in various fields of application: pharmaceutical, cosmetic, herbalist, food and beverage and not least of food waste [2-5]. Furthermore, the reproducibility of the extraction on the same matrix in weight terms was tested and comparison experiments were conducted with the other extraction techniques, which showed a higher recovery in favour of the extractor Naviglio, as well as a higher extract quality without alteration of thermolabile substances [6].

[1] D. Naviglio, *Anal. Lett*. **2003**, *36*, 1647-1659.

[2] M. Gallo, A. Formato, R. Giacco, G. Riccardi, D. Luongo, G. Formato, A. Amoresano, D. Naviglio, *Heliyon* **2019**, 5(4), e01526.

[3] M. Gallo, A. Formato, M. Ciaravolo, C. Langella, R. Cataldo, D. Naviglio, *European Food Research and Technology* **2019**, 245(8), 1767-1775.

[4] M.M. Salvatore, M. Ciaravolo, P. Cirino, A. Toscano, F. Salvatore, M. Gallo, D. Naviglio, A. Andolfi, *Separations* **2019**, 6(4), 50.

[5] D. Naviglio, A. Formato, M. Ciaravolo, G. Formato, M. Gallo, *Separations* **2020**, 7, 20.

[6] D. Naviglio, P. Scarano, M. Ciaravolo, M. Gallo, *Foods*. **2019**, *8*, 245.

Matrix removal and reaction cell approaches for the determination of trace elements in seawater by ICP-MS

Francisco Ardini[a], Marco Grotti[a]

[a] *Department of Chemistry and Industrial Chemistry, University of Genoa*

The determination of trace elements in seawater by inductively coupled plasma mass spectrometry (ICP-MS) is highly challenging, due to the low analyte concentrations (10^{-9}–10^{-12} mol L^{-1}) and strong spectral and non-spectral matrix effects. Non-spectral interferences are due to various reasons, such as salt deposition on the sampler cone orifice, physical effects related to the sample introduction system, ionization suppression due to the large amount of easily ionizable elements and space-charge effects. Spectral interferences are due to the formation of polyatomic ions in the plasma source, resulting from the saline matrix and the solvent. For example, $^{40}Ca^{16}O^+$, $^{40}Ar^{23}Na^+$ and $^{37}Cl^{16}O^+$ overlap with $^{56}Fe^+$, $^{63}Cu^+$ and $^{53}Cr^+$ ions, respectively, using quadrupole-based ICP-MS.

In this work, the matrix effects were mitigated by following different approaches, such as direct determination of 1:15 diluted seawater and separation/preconcentration procedures based on magnesium hydroxide coprecipitation assisted by aqueous ammonia or triethylamine (TEA). Then, the dynamic reaction cell (DRC) technique has been used to resolve the polyatomic interferences arising from the residual matrix, the solvent and plasma gases. For the optimization of the DRC conditions, several instrumental parameters have been taken into account, including reaction gas flow rate, rejection parameter q (RPq), axial field voltage (AFV), cell path voltage (CPV), quadrupole and cell rod offsets (QRO and CRO), and radiofrequency (RF). These parameters have been optimized by a multivariate experimental design, considering the use of two different reaction gases (NH_3 and O_2).

The dilution method, which had been already applied to the determination of As [1], allowed an accurate quantification of V in its oxide form ^{67}VO by using O_2 as reaction gas, as well as ^{55}Mn and ^{52}Cr by using NH_3 as reaction gas. The main drawback of this method is the degradation of the limits of detection due to the dilution step, but it is fast, simple, clean and requires small sample volumes (3.33 mL).

The coprecipitation method using aqueous ammonia had been already proven useful for ^{52}Cr, ^{54}Fe, ^{55}Mn, ^{208}Pb and $^{64,66,68}Zn$ [2], and here it provided good recoveries also for rare earth elements using O_2 as reaction gas. In addition, the coprecipitation procedure using TEA allowed the determination of ^{63}Cu, ^{52}Cr, ^{114}Cd and ^{58}Ni in different conditions, using NH_3 as reaction gas. Both these coprecipitation methods are simple, require a small quantity of clean reagents and provide a preconcentration factor of 10 (aqueous ammonia) and 5 (TEA).

The optimized methods have been finally applied to a number of seawater samples from the Ross Sea (Southern Ocean, Antarctica) collected during Austral summer 2020 in the framework of the PROPOSE (Processes controlling the presence and distribution of pollutants in Ross Sea Area) project of the National Program for Antarctic Research.

[1] M. Grotti, R. Frache, J. Anal. At. Spectrom. **2007**, *22*, 1481.
[2] F. Ardini, E. Magi, M. Grotti, *Anal. Chim. Acta* **2011**, *706*, 84.

Application of experimental design techniques for the optimization and the robustness study of photocatalytic degradation of emerging contaminants in water

Masho Hilawie Belay[a], Elisa Robotti[a], Maria Cristina Paganini[e], Claudio Medana[b], Federica Dal Bello[b], Marcello Manfredi[c,d], Sara Timo[a,d], Paola Calza[e,] Emilio Marengo[a]

[a] Department of Sciences and Technological Innovation, University of Piemonte Orientale, Viale Michel 11, 15121 Alessandria, Italy; [b]Department of Molecular Biotechnology and Health Sciences, University of Turin, Via Nizza 52, 10126 Torino, Italy; [c]Department of Translational Medicine, University of Piemonte Orientale, Via Solaroli 17, 28100 Novara, Italy; [d]Center for Translational Research on Autoimmune and Allergic Diseases, University of Piemonte Orientale, Corso Trieste 15/A, 28100 Novara, Italy; [e]Department of Chemistry, University of Turin, Via Giuria 7, 10124 Torino, Italy.

e-mail: masho.belay@uniupo.it

Recently, great attention has been paid to the spread of emerging contaminants in the environment and the development of strategies for their removal. In this framework, we present here a work which is part of the results obtained within the AQUAlity project (H2020-MSCA-ITN-2017 - Project N. 765860), devoted to developing an interdisciplinary cross-sectoral approach to effectively address the removal of contaminants of emerging concern from water. The work here presented deals with the optimization of the photocatalytic degradation of emerging contaminants in water. Experimental design techniques were applied to achieve two main goals: the optimization of the procedure and the identification of the robustness region around the nominal conditions.

The study was applied to two different contaminants of emerging concern: maprotiline, a tetracyclic antidepressant drug approved in many countries to treat depression associated with agitation or anxiety, and irinotecan, a chemotherapeutic agent most widely used for the treatment of colon, lung, and ovarian cancers. Maprotiline and irinotecan were selected as compounds of potential interest for further monitoring activities because of their frequent detections reported mostly in wastewater effluents and the knowledge gap on their fate and their transformation products in the aquatic environment. The photo-catalysis involved the use of a Ce-doped ZnO photocatalyst synthesized using a hydrothermal method, whose photocatalytic efficiency has been previously proved through tests carried out on phenol as a model compound and then maprotiline. Photocatalytic degradation under UV irradiation was performed using Philips Actinic BL TL-D lamps (290–400 nm range, 90±2 W m^{-2}) with a maximum emission at 365 nm.

The optimization involved 5 parameters: UV power, distance of the solution from the UV lamp, pH, concentration of the catalyst and concentration of the contaminant. For both molecules, a fractional factorial design was adopted with the addition of the star design and the experiments were evaluated at a fixed degradation time close to the half-time calculated at the center of the experimental domain.

The experimental response was given by the signal of the target molecule, the ratio C/C_0 (ratio between the concentration at the fixed degradation time with respect to the initial one) and the signal of all the identified degradation products. The target molecules and their degradation products were identified and quantified by HPLC-MS with an Orbitrap detector.

Multicriteria target functions were also exploited to identify the best conditions representing the best compromise between all the recorded experimental responses.

Optimization of Cd(II) sequestration by new sustainable polymer inclusion membranes

R. Di Pietro[a]*, C.Bretti*[a]*, P.Cardiano*[a]*, G. Lando* [a]
Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali CHIBIOFARAM, Università degli Studi di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina

Despite the availability of many chelating agents able to efficiently bind metal cations in solution, only few are actually viable as a large-scale countermeasure to contrast the problem of metal-polluted wastes. Among them, the non-biodegradable ethylenediaminetetraacetic acid (EDTA) ended up being overused becoming a pollutant itself, thus requiring novel approaches to remove metal cations from the environment [1]. Bearing this in mind, here we report preliminary results on a research aimed at the design and the development of new ecofriendly materials for efficient metal cations remediation in aqueous solution. Starting from the idea of employing a sustainable platform as matrix, a series of polymer inclusion membranes (PIMs), whose formulations is based on polylactic acid (PLA), Aliquat336 (Ali), as plasticizer, and a readily biodegradable chelating agent Citric Acid, have been prepared and tested for Cd(II) removal. It is worth to mention that the citric acid, being extensively employed in various fields, is often considered as an industrial byproduct, but it could be recovered and reused addressing the issue of waste disposal. In addition, citric acid was found to be potentially produced from biodegradable wastes [2]. Cd(II) sorption tests were selected by means of full factorial experimental design with two variables (pH and ionic strength) at three levels, to explore which cadmium chemical species is actually sorbed onto PIMs (i.e. Cd^{2+}, $CdCl^{+}$, $CdCl_3^{-}$, etc.) and to assess the effect of pH on sequestration. More in detail, the acid-base behavior of citric acid entrapped inside PIM was assessed by potentiometric titrations, in a pH range between 3 and 11 and ionic strength ranging from 0.1 and 3 mol dm^{-3} in NaCl. In addition, the Cd(II) sorption kinetics were investigated by means of differential pulse anodic stripping voltammetry (DP-ASV) in order to assess the time required to reach equilibrium. This information was then taken into account while performing isotherm experiments by DP-ASV. Infrared attenuated total reflectance (IR-ATR) spectroscopy investigations suggest the involvement of citric acid in the sorption process. The preliminary data obtained are encouraging and strongly indicate the potential of such PIMs for remediation purposes in aqueous solution.

References

[1] G. Lando, O. Gomez-Laserna, E. Proverbio, A. Khaskhoussi, D. Iannazzo, M. Rosaria Plutino, C. De Stefano, C. Bretti, P. Cardiano, *Environ. Sci. Pollut. Res.* 2021, **in press**, https://doi.org/10.1007/s11356-021-14328-0.

[2] O. Sawant, S. Mahale, V. Ramchandran, G. Nagaraj, A. Bankar, *J Microbiol Biotech Food Sci*; 2018, 8 (2) 821-828.

Optimization of an analytical procedure to determine nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) in the PM2.5

Annamaria Falgiani[a,b], *Giada Giglione*[a], *Flavio Vagnoni* [a], *Federico Girolametti* [a], *Matteo Fanelli*[a], *Cristina Truzzi*[a], *Silvia Illuminati*[a], *Anna Annibaldi*[a], *Lucia Cellini*[b].

[a] *Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, Via Brecce Bianche, 60131 Ancona, Italy*

[b] *ARPA Marche Dipartimento di Ascoli Piceno- Viale della Repubblica,34-63100- Ascoli Piceno – Italy.*

Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) are derivatives of polycyclic aromatic hydrocarbons (PAHs) which contains at least one nitro-functional group on the aromatic benzene ring of PAHs. Recent studies revealed that ~60% of nitro-PAHs are primarily found in the fine atmospheric particulate matter, i.e. $PM_{2.5}$ [1]. Nitro-PAHs determination in PM is very challenging since their concentrations are very low (pg or ng m^{-3}) in the atmosphere.

The present work aimed to validate an analytical procedure previously set-up and optimized (UNI EN 15549: 2008) for PAHs measurements to determine nitro-PAHs in the $PM_{2.5}$. $PM_{2.5}$ was sampled at the urban site of San Benedetto del Tronto (Ascoli Piceno, Italy) belonging to the Air Quality Survey Network of the Marche Environmental Protection Agency from February to December 2018. A total of 124 daily samples were collected by a low volume (daily volume of 55.2 m^3) sampler (HYDRA Inst.) onto 47 mm diameter quartz microfiber filters.

Collected filters were treated with deuterated surrogate standard (Benzo(a)anthracene d_12) and then subjected to a three-extractions procedure with toluene as organic solvent. Some samples were purified by thin layer chromatography (TLC) in 100 mL toluene/hexane mixture (1:1) as eluent. The extracts were analyzed by using a High-Performance gas chromatograph with a programmable temperature vaporization injection system (PTV) and a single quadrupole mass spectrometer. The quantification was obtained by the calibration curve method, with seven levels of concentrations from 0.02 ng/mL to 1.0 ng/ml. Two deuterated PAHs (PAHs-d: benzo[a]pyrene-d12, Perylene-d12) were added to the nitro-PAH solution as internal standards. The accuracy of the extraction method was evaluated through a recovery test, by spiking a half of the blank filter with known amount of nitro-PAHs standard solutions (1-Nitronaphthalene, 2-Nitronaphthalene, 9-Nitrophenanthrene, 5-Nitroacenaphthene, 2-Nitrofluorene, 2,7-Dinitrofluorene, 1-Nitropyrene, 6-Nitrocrisene, 7-Nitrobenz(a)anthracene, 6-Nitrobenzo(a)pyrene) and of internal standard. The percentage of recovery exceeded 80% for all target compounds except for the 6-nitrobenzo[a]pyrene. The linearity of the response was evaluated over the range 0.02 ÷ 1 ng mL^{-1}, by using six concentration levels and three replicates for each level. The limit of detection (LOD) was 0.02 ng mL^{-1}.

Finally, the validated method was applied to real $PM_{2.5}$ samples. An increase of nitro-PAH was observed during summer season. Among the studied nitro-PAH the 1-Nitropyrene resulted as the most abundant compound. Several studies reported the 1-Nitropyrene as indicator for ship emissions [2]. San Benedetto del Tronto is an important touristic site and during summer is subjected to a consistent maritime traffic resulting in the 1-nitro pyrene increase.

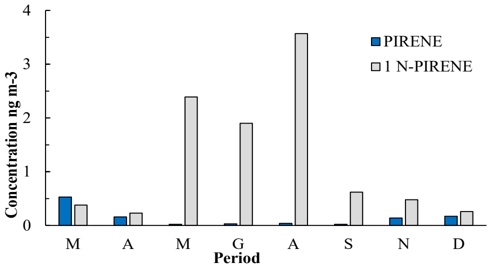


Fig. 1. PAH and nitro-PAH evolution during the sampling

[1] Albinet A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., Jaffrezo, J.L., *Atmos. Environ.* **2008**, *42*, 55–64.

[2] ZhaoJ., Zhang Y., Wang T., Sun L., Yang Z., Lin Y., Chen Y., Mao H. *Chemosphere*, **2019**, *225*, 43-52.

Making artificial snow in a cold room at -30°C for photochemical investigations

Stefano Frassati, Luca Carena, Fabrizio Sordello, Marco Minella, Claudio Minero*

[a] Dipartimento di Chimica, Università degli Studi di Torino, Torino, Italy

Stefano.frassati@edu.unito.it

The investigation of (photo)chemical reactions in/on snow/ice has been the subject of some studies in the last twenty years. Data about snow/ice photochemistry that are reported in the literature are often affected by quite wide variability, mainly because of the scarce reproducibility in the preparation of snow/ice samples for irradiation experiments. The comparison among results coming from different works is usually difficult, because of the dissimilar procedures and conditions adopted to make snow/ice in the lab. We tested different methods for snow samples preparation inside a cold room set at 243 K, to get a good reproducibility of photochemical experiments, as analytical outcomes, mostly time-dependent, are very dependent on the matrix.

A widely used technique to make ice samples entails the freezing aqueous solutions directly inside vials, which are then put under a suitable lamp for irradiation [1]. Alternatively, once it is formed, ice is broken and then irradiated. However, the main issue with these two approaches is the assumption that photoreactions in/on snow are similarly to those occurring in/on ice. In addition, depending on the chemical species present in the system, the analyte partitioning within the ice was observed [2]. Another used technique is the 'fast freezing', namely the nebulization of aqueous samples directly in liquid N_2 (77 K) by means of an airbrush [3]. The fast frozen snow is then transferred inside a cold environment to conduct photochemical studies. However, snow samples made with this approach can be highly affected by atmospheric humidity and temperature change (from 77 K of liquid nitrogen possibly to room temperature). This uncontrolled procedure could trigger unidentified metamorphism processes that could affect snow photochemistry. Additionally, this method requires large consumption of liquid N_2.

Making snow samples inside a large cold room at 243 K is a good alternative to overcome the problems described above. Here the temperature and atmospheric humidity are controlled by the large cold room, which avoids temperature variations. In this setup the parameters to be monitored are the nebulization flow and the distance between the sprayer and the reservoir where snow samples are collected. This approach allowed the preparation of snow samples suitable for irradiation experiments with a good reproducibility when photodegradation of furfuryl alcohol in the presence of Rose Bengal (RB) was carried out. RB is a well-known photosensitizer for singlet oxygen [4] under the visible irradiation. During this process we observed loss of chemical species. This loss was assessed using four different compounds (sodium nitrate, Rose Bengal, furfuryl alcohol and phenol), showing that ions concentration remains unchanged passing from nebulized liquid to melted snow samples, while neutral molecules were partially lost during snow production.

This preliminary work posed the basis to carry out reproducible photochemical investigations in/on snow, which are significant for the impacts/role of environmental proxies and pollutants in polar regions, as it will be described in another work presented in this congress.

[1] T. Hullar, D. Magadia, C. Anastasio, *Environ. Sci. Technol.*, **2018**, 52, 12225.
[2] P. P. A. Malley, J. N. Grossman, T. F. Kahan, *J. Phys. Chem. A*, **2017**,121, 7619.
[3] D. Heger, J. Klánová, P. Klán, *J. Phys. Chem. B*, **2006**, 110, 1277.
[4] J. P. Bower, C. Anastasio,, *Atmos. Environ.*, **2013**, 75, 188.

Trace elements in a stratified estuarine environment: behaviour along the water column and mobility at the sediment-water interface (Gulf of Trieste, northern Adriatic Sea)

E. Pavoni[a], A. De Marchi[a], E. Petranich[a], F. Floreani[a], M. Crosera[b], J. Faganeli[c], S. Covelli[a], G. Adami[b]

[a] *Dipartimento di Matematica e Geoscienze, Università degli studi di Trieste, Trieste, Italia*
[b] *Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli studi di Trieste, Trieste, Italia*
[c] *Marine Biology Station, National Institute of Biology, Pirano, Slovenia*

Sediments often act as reservoirs of contaminants, but they can also be considered a secondary source of contamination due to remobilisation processes at the sediment-water interface (SWI) which may affect the quality of the overlying water and aquatic biota [1,2]. The estuarine system of the Timavo/Reka River is located in the Gulf of Trieste (northern Adriatic Sea) and the innermost sector of the estuary was recognised as the most critical area. There, elevated concentrations of potentially toxic trace elements (PTEs) were detected in surface sediments and the scarce water circulation led to a permanent oxic-hypoxic interface along the water column [3].

This research aims at understanding if and how biogeochemical processes may affect PTE (As, Cr, Hg, Fe, Mn, Ni, Pb, V) mobility and related fluxes at the SWI. Sampling activities were performed before (June) and after (September) the forced aeration by means of a system of porous pipes laid on the bottom with the aim to re-oxygenate the water column in summer. Water aliquots were sampled along the water column, short sediment cores were collected to investigate the solid (sediments) and dissolved (porewater) phases and *in situ* benthic chamber experiments were conducted at the SWI.

Results showed that the water column was oxygen stratified and hypoxic conditions were observed in the bottom water layer, mostly in June (2.29 mg/L of dissolved oxygen) when reductive conditions also occurred (-58 mV). Consequently, dissolved PTE concentrations increased with increasing depth and were maximum at the bottom due to dissolution/desorption processes involving Fe and Mn oxy-hydroxides [4]. A gradual oxygen depletion was also observed inside the chamber during the benthic chamber experiments testifying to organic matter remineralisation processes and subsequent increase of dissolved PTEs.

Regarding PTE profiles in porewater, the highest PTE concentrations were observed in June, especially at the top of the sedimentary sequence implying that hypoxic conditions may promote the release of PTEs at the SWI.

[1] C. Caplat, H. Texier, D. Barillier, C. Lelievre, *Mar. Pollut. Bull.* **2005**, *50*, 504–511.
[2] E. Petranich, S. Croce, M. Crosera, E. Pavoni, J. Faganeli, G. Adami, S. Covelli, *Environ. Sci. Pollut. R.* **2018**, *25*, 26887–26902.
[3] E. Pavoni, M. Crosera, E. Petranich, J. Faganeli, K. Klun, P. Oliveri, S. Covelli, G. Adami, Estuar. Coast *in press* **2021**, DOI: 10.1007/s12237-021-00910-9.
[4] O. Dellwig, T. Leipe, C. März, M. Glockzin, F. Pollehne, B. Schnetger, E.V. Yakushev, M.E. Böttcher, H.J. Brumsack, *Geochim. Cosmochim. Ac.* **2010**, *74*, 7100–7115.

How to clean and safely remove fluoride from solutions after HF-based acid digestion: a microwave-assisted vessel-inside-vessel protocol

M. Pinna [a], D. Spanu [a], G. Binda [a], C. Dossi [a] and S. Recchia [a]

[a] Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, via Valleggio 11, 22100 Como, Italy.

Microwave-assisted acid digestion is a routine technique for solid sample dissolution for subsequent elemental composition or isotope ratio analysis. A mixture of pure acids is commonly placed in a polymeric container (e.g., PFA, PTFE) and then treated with microwave radiation to reach high temperature and pressure needed for sample dissolution. The choice of the acid mixture is strongly related to the nature of the sample matrix. For instance, the dissolution of silicate-containing materials (e.g., minerals) normally requires the employment of hydrofluoric acid (HF) as it can efficiently dissolve them and act as a strong complexing agent for various metals [1]. Although fundamental for such applications, the use of HF poses serious issues for subsequent elemental analysis making necessary its removal after acid digestion. In more detail, the precipitation of insoluble salts (e.g., with Ca, Al, Mg) and the corrosivity of HF towards glass/quartz (the most used materials to build up instrumental glassware) are not compatible with conventional trace element quantification method. At present, hot displacement with HCl or HNO_3 is still the most used method for HF elimination, but this evaporation procedure presents a problem: due to safety reasons it is necessary to operate under a chemical hood largely increasing the risk of contamination processes and thus possibly compromising the accurate quantification of elements at the ultra-trace level. Alternatively, H_3BO_3 could be used to form HBF_4, which is not corrosive towards glass or quartz, but it causes severe spectral interferences in ICP-OES on many elemental determinations [2]. Owing to the current lack of a safe and clean way to eliminate HF after mineralization, we decided to develop a vessel-in-vessel procedure envisaged to fill this gap. As recently reported by some of us, this technique strongly reduces sample contaminations caused by PTFE memory effects [3]. Briefly, the smaller PFA vessel is filled with the sample to be digested, loosely closed, and then put into a commercial PTFE vessel containing few milliliters of ultrapure water (or a specific scavenging solution, e.g. NaOH, $Ca(NO_3)_2$). After a microwave irradiation cycle (mineralization step) the migration of HF from the inner vessel to the outer one was observed (mean fluorides removal = 34 ± 7%). Such decontamination process is reasonably ascribed to the vaporization of HF and its dissolution in the outer solution. Aiming to further remove fluorides, additional microwave cycles were performed over the same sample solution. Parameters such as the number of microwave cycles, microwave cycle time, volume and composition of fluoride scavenger solution were optimized. Optimized conditions allow to remove more than 80% of HF by performing three times a 20-minutes long MW irradiation cycle. Such result enables the direct analysis of the diluted sample solution without requiring additional treatments. Considering that all sample manipulations are performed under a laminar flow hood on cold solutions, the proposed method is suitable to perform acid digestions for ultra-trace elemental determinations, in all cases where the utilization of HF is mandatory.

[1] C. Moor, T. Lymberopoulou, V.J. Dietrich, *Microchim. Acta* **2001**, *121*, 123-128.
[2] J. Fucskó, S. H. Tan, H. La, M. K. Balazs, *Appl. Spectrosc.* **1993**, *47 (2)*, 150-155
[3] D. Spanu, L. Butti, G. Boldrocchi, R. Bettinetti, D. Monticelli, *Anal. Sci.* **2020**, *36 (7)*, 889-892

Using Controlled Periodic Illumination to Evaluate the Photocatalytic Activity of Aqueous TiO_2 Suspension

Prozzi Marco [a], Sordello Fabrizio [a], Pellegrino Francesco [a,b] and Valter Maurino [a,b]

[a] *Department of Chemistry, University of Torino, Torino, Italy;* [b] *JointLAB UniTo-ITT, Torino, Italy*

The multiplicity and heterogeneity of phenomena that occur during substrate degradation in heterogeneous photocatalysis, together with the great number of experimental variables that may affect the observed degradation rate, hinder the evaluation of the intrinsic activity for a certain photocatalyst [1].

Controlled Periodic Illumination (CPI, see **Figure 1.a**) was firstly investigated in the field of TiO_2 photocatalysis as a strategy to improve the photocatalytic performance of the process [2].

Although it is now established that this technique, when applied on bare TiO_2, is not able to enhance the quantum yield (η) of the photocatalytic system [3], we suggested the possibility to employ CPI to obtain kinetic information undoubtedly related to the catalyst activity. In fact, if the photocatalyst works in the recombination regime (i.e. $\eta \rightarrow 0$), then there is a formal equivalence between two very different physical system: it is possible to quantitatively describe the substrate photocatalytic oxidation with the theory of intermittent illumination, originally developed for homogeneous photopolymerization processes [4].

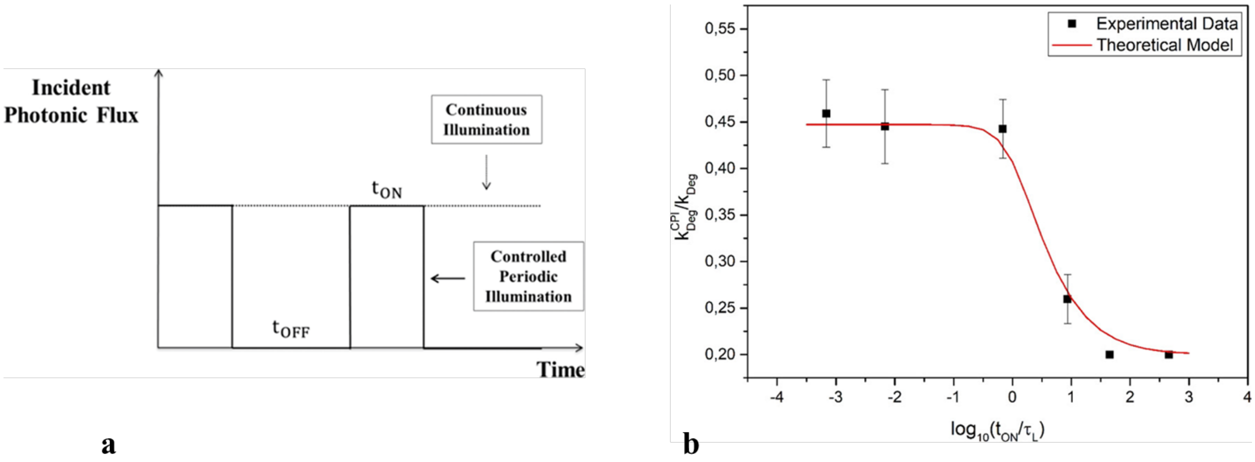


Figure 1. a) Photonic flux incident on the reaction cell during Continuous Illumination (dashed line) and Controlled Periodic Illumination experiment (solid line) where t_{ON} and t_{OFF} are, respectively, the light time and the dark time. b) Theoretical model and experimental data for the ratio between the substrate degradation rate under CPI and Continuous Illumination conditions versus the base 10 logarithm of the ratio between the light time and the lifetime of active species (τ_L) .

Hence, through a non – linear regression procedure on the experimental data for continuous and CPI experiments (**Figure 1. b**), it is possible to extract the lifetime of active species involved in substrate degradation. Starting from this kinetic information, a Photocatalytic Activity Index can be defined: it is the ratio between the kinetic constant for substrate oxidation and the kinetic constant for charge carrier recombination.

[1] C. Minero, D. Vione, *App. Catal. B: Environmental*. **2006**, 67, 257.
[2] J. G. Sczechowski, C. A. Koval, R. D. Noble, *J. Photochem. Photobiol. A*, **1993**, 74, 273.
[3] C. J. G. Cornu, A. J. Colussi, M. R. Hoffmann, *J. Phys. Chem. B*, **2001**, 105, 1351.
[4] G. M. Burnett, H. W. Melville, *Nature*. **1945**, 156, 661.

Voltammetric study for the determination of Diclofenac in aqueous solutions using electro-activated carbon electrodes

Silvia Berto[a], Enrico Prenesti[a], Emanuele Terranova[a], Enrico Cagno[a], Mery Malandrino[a], Agnese Giacomino[b], Luca Carena[a], Davide Vione[a,c], Ornella Abollino[b].

[a] Department of Chemistry, University of Turin, via P. Giuria 7, 10125 Turin, Italy; [b] Department of Drug Science and Technology, University of Torino, Via P. Giuria 9, 10125 Turin, Italy; [c] INSTM and NIS Centre, University of Turin, via Quarello 15A, 10135 Turin, Italy.

Diclofenac (2-[(2,6-dichlorophenyl)amino]benzeneacetic acid sodium salt; hereafter, DCF) is a non-steroidal anti-inflammatory drug with high activity and considerable tolerability, widely used as pain and inflammation reliever. Yearly DCF consumption by humans was estimated to be ~ 1443 tons globally [1]. Consequently, DCF was detected in different environmental compartments. The technical report published by the European Joint Research Centre [2] showed a detection frequency of DCF above 50% and a mean DCF concentration value equal to 66 ng L^{-1} in surface waters. A fast detection of DCF in the effluent of wastewater treatment plants would allow estimating the drug contamination level, which could help immediate decision-making.
Voltammetry is an analytical technique that may answer the requests of low cost, high sensitivity and potential portability required by a screening method. In this work, a process of anodic electro-activation was applied to the electrochemical determination of DCF in water samples. The procedure was applied in previous works [3,4] on glassy carbon electrodes (GCEs) and requires the application of an anodic potential for a defined time to the GCE immersed in a borate-phosphate buffer solution at pH 9. The electrochemical behaviour of DCF was here studied on both GCE and screen-printed carbon electrodes (SPCEs) after anodic activation. The anodic activation conditions were thus optimized for the SPCE as well and the activation was found to enhance the DCF signals in both cases. Most of the measurements were conducted in a phosphate buffer at pH 2, because the voltammetric response of DCF is higher in acidic solutions. Three voltammetric peaks could be detected, an anodic one at ~0.8 mV, corresponding to the DCF oxidation, and two almost reversible peaks at a lower voltage, due to a by-product of DCF oxidation. Differential Pulse Voltammetry (DPV) was used and optimized by Experimental Design (DoE) method for the determination of DCF. The linearity range of the response as well as the calibration and limit (namely, LoD and LoQ) parameters were defined. The DPV measurements optimized on GCE take advantage of the adsorption properties of the oxidation by-product. Indeed, a pre-oxidation step was conducted on a solution of DCF, and the cathodic signal of the adsorbed by-product was then detected. The peak current increased linearly with the concentration in the range $1\cdot10^{-8}$ - $7\cdot10^{-8}$ mol L^{-1}. Instead, the procedure based on SPCE allows for recording the peak current due to the direct oxidation of DCF. Both solution and drop measurement conditions were optimized, reaching good repeatability. The peak current increased linearly with the concentration in the range $2\cdot10^{-8}$ - $4\cdot10^{-7}$ mol L^{-1}, and the LoD values were $9\cdot10^{-9}$ and $2\cdot10^{-8}$ mol L^{-1} for solution and drop measurements, respectively.

[1] V. Acuña, A. Ginebreda, J.R. Mor, M. Petrovic, S. Sabater, J. Sumpter, D. Barceló, *Environ Int*. **2015**, *85*, 327.
[2] R. Loos, D. Marinov, I. Sanseverino, D. Napierska, T. Lettieri, *Review of the 1st Watch List under the Water Framework Directive and recommendations for the 2nd Watch List. Joint Research Center.* **2018**.
[3] E. Chiavazza, S. Berto, A. Giacomino, M. Malandrino, C. Barolo, E. Prenesti, D. Vione, O. Abollino, *Electrochim. Acta* **2016**, *192*, 139.
[4] S. Berto, L. Carena, F. Valmacco, C. Barolo, E. Conca, D. Vione, R. Buscaino, M. Fiorito, C. Bussi, O. Abollino, M. Malandrino, *Electrochim. Acta* **2018**, *284*, 279.

Chemometric approach for the study of Fiber Optics Reflectance spectroscopy (FORS) spectra as a marker of different azo dyes

Tiziana Forleo[a], Maria Cristina Caggiani[b], Giulio Pojana[b], Giovanni Lagioia[c], Annarosa Mangone[a,d], Lorena Carla Giannossa[a,d]

[a] Dipartimento di Chimica, Università di Bari Aldo Moro, via Orabona 4, 70126 Bari, Italy
[b] Dipartimento di Filosofia e Beni Culturali, Università Ca' Foscari, Dorsoduro 3246, 30123 Venezia, Italy
[c] Dipartimento di Economia, Management e Diritto dell'Impresa, Largo Abbazia Santa Scolastica, 70124 Bari, Italy
[d] Centro Interdipartimentale Laboratorio di Ricerca per la Diagnostica dei Beni Culturali, Università di Bari Aldo Moro, via Orabona 4, 70126 Bari, Italy.

Fiber Optics Reflectance Spectroscopy (FORS) is a non-invasive and non-destructive analytical technique, and thanks to its portability for on-site and in situ samples analysis, is commonly used to study works of art[1,2]. The samples characterized by FORS are natural textiles colored by azo dyes, synthesized by Leopoldo Cassella & Co. firm at the end of the 19th century - beginning of the 20th century, a distinctive period that marks the transition from natural dyes to synthetic ones on a large scale. Items are part of two pattern books of textiles - "Diaminfarben auf halbseide. (Seide und Baumwolle)/Diamine colors on half silk. (Silk and cotton)" (no date reported) and "Les Couleurs Diamine dans la teinture des tissus mi-laine/Diamine Colors in the dyeing of mid-wool fabrics" (1900)- coming from the Commodity Science Museum of the Department of Economics, Management and Business Law at the University *Aldo Moro* of Bari (Italy). The declared dye concentration in silk-cotton blend textiles is 2% for almost all samples with few exceptions (0,25%: 2 dyes, 1%: 2 dyes, and 6%: 2 dyes). In the case of wool-cotton blend textiles, two concentrations (2% and 0.75%) are reported for each dye selected and both were analyzed.
Also, two multivariate methods, the Principal Component Analysis (PCA) and the Partial Least Square Discriminant Analysis (PLS-DA) were employed to explore, discriminate and classify samples based on the spectral profile[3,4]. The combination of chemometric methods and FORS characterization demonstrates the recognizability of the dyes despite aging and sets the stage for a database of azo dyes based on the FORS profile.

Fig. 1 FORS analysis ongoing on textiles of Leopold Cassella & Co. pattern books analyzed.

[1] de Ferri L, Tripodi R, Martignon A, Ferrari ES, Lagrutta-Diaz AC, Vallotto D, Pojana G. Non-invasive study of natural dyes on historical textiles from the collection of Michelangelo Guggenheim. *Spectrochim Acta A*, **2018;** 204: 548-67
[2] Gulmini M, Idone A, Diana E, Gastaldi D, Vaudan D, Aceto M. Identification of dyestuffs in historical textiles: Strong and weak points of a non-invasive approach. *Dyes Pigments*, **2013**; 98: 136-45.
[3] Brereton, R.G.Chemometrics for Pattern Recognition; Wiley: Hoboken, NJ, USA, **2009**; ISBN 9780470987254.
[4] Ballabio, D.; Consonni, V. Classification tools in chemistry. Part 1: Linear models. PLS-DA. *Anal. Methods*, **2013**, 5, 3790–3798.

A paper-printed electrochemical device based on bi-enzymatic detection of glucosinolates in food waste

Noemi Colozza [a], Angelica Mucaria [a], Fabiana Arduini [a,b], Danila Moscone [a]

[a] *University of Rome Tor Vergata, Via della ricerca scientifica, Roma, Italia*
[b] *Sense4Med, Via Renato Rascel 30, Roma, Italia*

Glucosinolates belongs to a class of phytochemical compounds present in the Brassicaceae family, including mustard, cabbage, and horseradish. Their chemical structure is composed by a glucose unit and a sulfonate oxime, linked together by a sulphur atom, with an organic side group that determines the specific biological activities. When a plant is damaged (e.g. by a herbivorous), glucosinolates play an important role in the plant's defenses: they are hydrolysed by myrosinase enzyme (thioglucoside glycohydrolase) and induce toxic effects on the predator. Interestingly, glucosinolates have shown antioxidant properties in humans and can reduce the risk of cardiovascular diseases [1]. However, the European Commission recommended to avoid an excessive intake of glucosinolates, because of possible negative interferences with the endocrine system [2].

Thus, the monitoring of glucosinolate levels into Brassicaceae turns to be a matter of interest in the agri-food field. The reference methods require first the extraction of glucosinolates from the plant sample by boiling in protic solvents and then their analysis through chromatographic techniques coupled with a mass spectrometer or a UV-visible spectrophotometer. Besides these complex, expensive and reagent/time consuming methods, smarter innovative approaches have been proposed, such as the development of biosensors.

In this work, a paper-printed sensor for glucosinolate was developed basing on a bi-enzymatic detection principle. Indeed, the combined use of myrosinase and glucose oxidase enzymes was shown to be a promising approach for the indirect measurement of glucosinolates [3,4], consisting in measuring glucose that is hydrolysed by myrosinase. Herein, glucose oxidase and myrosinase were easily immobilised on two separate filter paper pads by simple absorption into the cellulose network. The paper pads were overlapped onto a paper-printed graphite-based sensor, previously modified with a carbon black/Prussian blue nanocomposite. The well-known properties of Prussian blue [5] allow the electroanalytical performances to be significantly improved toward the measurement of hydrogen peroxide as enzymatic by-product of glucose oxidase. After having verified the enzymatic behaviour of both the enzymes absorbed on the paper support (overall $K_M = 5.2 \pm 0.9$ mM), standard amounts of glucosinolates (i.e. sinigrin) were detected with a LOD of 0.03 mM in amperometric mode. Moreover, the sensor was applied for the analysis of extracted samples from several species of Brassicaceae.

[1] S. Novío, M. E. Cartea, P. Soengas, M. Freire-Garabal, M. J. Núñez-Iglesias, *Molecules* **2016**, 21(5), 626.
[2] S. Wooding, H. Gunn, P. Ramos, S. Thalmann, C. Xing, W. Meyerhof, *Chem. senses* **2010,** 35(8), 685-692.
[3] A. Koshy, H. P. Bennetto, G. M. Delaney, A. J. MacLeod, J. R. Mason, J. L. Stirling, C. F. Thurston, *Anal. Lett.* **1988,** 21(12), 2177-2194.
[4] B. Wu, G. Zhang, S. Shuang, C. Dong, M. M. Choi, A. W. Lee, *Sens. Actuat. B-Chem* **2005**, 106(2), 700-707.
[5] S. Cinti, F. Arduini, G. Vellucci, I. Cacciotti, F. Nanni, D. Moscone, *Electrochem. Comm.* **2014**, 47, 63-66.

Acknowledgements to PRIN 2015 FFY97L for funding.

Compact miniaturized bioluminescence sensor based on continuous air-segmented flow for real-time monitoring: application to bile salt hydrolase (BSH) activity and ATP detection in biological fluids.

V. Marassi[a], *A. Roda*[a,b], *P. Greco*[c], *Simoni*[d], *G. Moroni*[e], *A. Gioiello*[e], *B. Roda*[a,b]

[a] *Department of Chemistry G.Ciamician, Alma Mater Studiorum-University of Bologna, Italy;* [b] *INBB – Biostructures and Biosystems National Institute-Rome, Italy;* [c] *Department of Life Sciences, University of Modena and Reggio Emilia-Italy;* [d] *Department of Medical and Surgical Sciences, Alma Mater Studiorum-University of Bologna, Italy;* [e] *Department of Pharmaceutical Sciences, University of Perugia-Italy*

A simple and versatile continuous air-segmented flow sensor using immobilized luciferase was designed as a general miniaturized platform based on sensitive biochemiluminescence detection.

The device employs miniaturized microperistaltic pumps to deliver flows and compact sensitive light imaging detectors based on BI-CMOS (smartphone camera) or CCD technology. The low-cost components and power supply make it suitable as out-lab device at point-of-need to monitor kinetic-related processes or ex-vivo dynamic events. A nylon6 flat spiral carrying immobilized luciferase was placed in front of the detector in lensless mode using a fiber optic tapered faceplate.

As a proof of concept to demonstrate the system's broad applicability, we developed two bioassay formats: the ex-vivo measurement of ATP in the brain's extracellular environment, also in hyphenation with microdialysis systems, and the quantification of microbiome bile salt hydrolase (BSH) activity via BL detection of aminoluciferin in human stool [1].

ATP was measured in samples collected by microdialysis from rat brain with detection levels as low as 0.4 fmoles. For the evaluation of bile salt hydrolase (BSH) activity in intestinal microbiota, the same platform was used with a luciferin derivative. An aminoluciferin was conjugatated with chenodeoxycholic acid forming the amide derivative aLuc-CDCA. The hydrolysis of the aLuc-CDCA probe by BSH releases free uncaged aminoluciferin which is the active substrate for luciferase leading to light emission. This method can detect as low as 0.5 mM of aLuc-CDCA, showing promise for the application to real faecal human samples to study BSH activity and its modulation by diseases and drugs.

[1] Roda, A.; Greco, P.; Simoni, P.; Marassi, V.; Moroni, G.; Gioiello, A.; Roda, B. *Chemosensors.* **2021**, *9*, 122.

Poster presentation
Barbara Roda 3383538051

Layered (as hydrotalcite-like) compound synthesized, characterized and used to build new sensor and biosensor for checking hydroperoxides

Mauro Tomassetti [a,b]*, Riccardo Pezzilli* [c]*, Giuseppe Prestopino* [c]*, Corrado Di Natale* [a]*, Pier Gianni Medaglia* [c] *and Luigi Campanella* [b]

[a] *Department of Electronic Engineering, University of Rome ''Tor Vergata'', Viale del Politecnico 1, 00133, Rome, Italy.* [b] *Department of Chemistry, University of Rome, "La Sapienza", P.le A. Moro 5, 00185, Rome, Italy.* [c] *Department of Industrial Engineering, University of Rome ''Tor Vergata'', Viale del Politecnico 1, 00133, Rome, Italy.*

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, or anionic clays [1], are an important class of lamellar materials described by the general formula $[M^{II}_{1-x} M^{III}_{x} (OH)_2]^{x+}[A^{m-}]_{x/m}\cdot n\, H_2O$, where M^{II} and M^{III} represent metallic cations and A^{m-} the interlayer anion. The LDH is assembled by periodically stacking (M^{II}, M^{III}) $(OH)_2$ octahedral layers, whose positive charge is balanced by the negative one of intercalated anions embedded between the positively charged octahedral layers. A certain number of H_2O molecules are also contained in these interlayers, so that the entire structure can swollen like gel, increasing the content of water molecules. Many applications have been proposed in the recent years for LDHs [2,3]: drug carriers, absorbents, cation removal, inorganic catalysts, energy harvesting, electrochemical applications, biosensors. Since our interest is in sensors and biosensors, in this research we decided to investigate the real possibilities of using $[Zn^{II} Al^{III} (OH)_2]^{+} NO_3^{-}$ (LDH), to build both an electrochemical enzyme catalase biosensor and a simple catalytic sensor, for the determination of hydroperoxides, such as hydrogen peroxide. To this purpose we both took into account what is reported in the literature to this regard, and conceived new solutions, with respect to electrochemical biosensors already proposed by other authors [4-6]. A sensor system based on a glassy carbon (GC) electrode modified with Layered double hydroxide (LDH) $[Zn^{II} Al^{III} (OH)_2]^{+} NO_3^{-}$ (with, or without, the addition of an enzyme cross-linked in the LDH matrix), which was strongly fixed on the GC by silver paste, has been fabricated . By means of XRD, thermal analysis and cyclic voltammetry it has been shown that catalase enzyme interacts by intercalating at least partially with LDH; this immobilization was then reinforced by cross-linking with glutaraldehyde. Main virtue of new two devices sems to be a very long duration, not less than at least two and a half months, in operative conditions. A limit of detection (LOD) to hydrogen peroxide of the enzyme catalase biosensor was about 0.20 mM. Also, the same electrode without catalase enzyme, but with LDH glued on GC, showed catalytic activity towards H_2O_2, exhibiting an amperometric response obviously lower than that of the enzyme electrode, with a LOD of about 1.0 mM. Since, the two sensors have different but almost consecutive linearity ranges, there is therefore the possibility of determining hydrogen peroxide over a wide range of concentrations (between about 0.2 and 1200 mM). In conclusion on the basis result of this research LDH seems an effective material and more than satisfactory to build both simple catalytic sensors and enzyme biosensors.

[1] C. Forano, U. Costantino, V. Prévot, C.T. Gueho. Layered Double Hydroxides (LDH). In *Developments in Clay Science*; Elsevier, **2013**; Vol. *5*, pp. 745–782 ISBN 978-0-08-099364-5.
[2] G. Arrabito, A. Bonasera, G. Prestopino, A. Orsini, A. Mattoccia, E. Martinelli, B. Pignataro, P.G. Medaglia, *Crystals* **2019**, *9*, 361.
[3] X. Bi, H. Zhang, L. Dou, *Pharmaceutics* **2014**, *6*, 298.
[4] D. Shan, S. Cosnier, C. Mousty, *Anal. Chem.* **2003**, *75*, 3872.
[5] C. Mousty, L. Vieille, S. Cosnier, *Biosens. Bioelectron.* **2007**, *22*, 1733.
[6] D. Shan, Y. Wang, M. Zhu, H. Xue, S. Cosnier, C. Wang, *Biosens. Bioelectron.* **2009**, *24*, 1171.

The Coupling of Silver Thiolate×Non-aqueous Reversed Phase Retention Mechanisms for the Elucidation of Triacylglycerol Profile in Borage Seed Oil Samples

Paola Arena [a], *Danilo Sciarrone* [a], *Paola Dugo* [a,b], *Paola Donato* [c], *Luigi Mondello* [a,b,d]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[c] *Department of Biomedical, Dental, Morphological and Functional Imaging Sciences, University of Messina, Messina, Italy;*
[d] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

Among lipid species, triacylglycerols (TAGs) are the main components of edible oils and animal fats; they consist of three fatty acids (FAs) esterified to a glycerol moiety (positions sn-1, 2 and 3) and can be viewed as concentrated stores of metabolic energy.

Each lipid matrix shows a unique TAG profile which can serve as fingerprint to ensure the quality and authenticity of food products.

Complex lipids have been extensively investigated by means of liquid chromatography (LC) coupled to mass spectrometry detection, being silver ion (Ag^+)- and non-aqueous reversed phase-LC (NARP-LC) the most suitable approaches for TAG separation. In particular, separations by Ag^+-LC depend upon TAG unsaturation degree and double bounds position, while in NARP-LC TAGs elute according to the increasing partition number (PN), defined as the total carbon number (CN) minus two times the number of DBs (PN = CN-2DBs).

However, for the analysis of complex food samples, consisting of different lipid species, a combination of two or more separation modes may be recommendable, aiming at enhancing the resolving power of the chromatographic system; to this regard, NARP-LC and Ag^+-LC separation mechanisms can be conveniently coupled thanks to their complementarity.

In this research, the TAG profile of borage (*Borago officinalis*) seed oil was obtained by two-dimensional comprehensive liquid chromatography (LC×LC), by the coupling of silver thiolate and octadecylsilica monodisperse materials. Concerning the first dimension, a prototype silver thiolate chromatographic material was investigated, offering many advantages as higher stability, longer operational life, controlled silver content and reproducibility across extended use.

The highest orthogonal selectivity of the two separation dimensions afforded a useful fingerprint-type distribution of the lipid components, characteristically located into the 2D space according to their DB values (in the 0-9 range) and PN values (in the 36-56 range).

A total of 94 TAG compounds were identified in borage oil by ion trap-time of flight detection, using atmospheric pressure ionization.

Investigation of the Phenolic Compounds Occurring in Leaves and Fruits of Olive Trees (*Olea europaea*) and in Extra Virgin Olive Oil and its Byproducts Using RP-HPLC Methods Developed by a Computer Assisted Design-of-Experiments (DoE) Approach

Mohamed S. Daas[a], *Massinissa Faci*[a,b], *Isabella Nicoletti*[c], *Malika Douzane*[a], *Danilo Corradini*[c]

[a]Food Technology Research Division, National Institute of Agronomic Research of Algeria, 02 Frères Ouaddek Avenue, 16200 Algiers, Algeria; [b]Faculty of Biological and Agronomic Science, University Mouloud Mammeri, Krim Belkacem Boulevard, 15000 Tizi-Ouzou, Algeria; [c]CNR, Institute for Biological Systems, Area della Ricerca di Roma 1, 00015 Montelibretti (Rome), Italy (danilo.corradini@cnr.it).

The agronomic management of olive trees (Olea europaea) and the olive processing industry generate a large quantity of byproducts, which might either create major environmental problems or become a source of novel bioactive compounds for the pharmaceutical, nutraceutical and cosmetic industry. Most of them are phenolic compounds, which are a large class of plant secondary metabolites comprising a great number of heterogeneous structures, ranging from simple molecules to highly polymerized compounds. Phenolic compounds in plant tissues occur mostly as soluble conjugates and insoluble forms, covalently bound to sugar moieties or cell wall structural components. They play important roles in the plant defense system against pathogenic attacks and environmental stresses and may confer specific sensory characteristics to food from plants, whose botanical and geographical origin may be related to their occurrence and amount. Thus, phenolic compounds are also potential chemical markers for the evaluation of botanical and geographical origin of plant-derived food products and dietary supplements. Moreover, as other plant secondary metabolites, phenolic compounds have evidenced to exhibit several biological activities and health benefits against chronic and degenerative human diseases.

A variety of instrumental analytical separation techniques are employed to identify and quantify each of the main phenolic compounds occurring in plants and plant-derived food products. Among them, high performance liquid chromatography, mostly in reversed phase separation mode (RP-HPLC), is the techniques of choice [1]. This communication describes the development of computer assisted RP-HPLC methods for the separation, identification, and quantification of phenolic compounds extracted from representative samples of the oil production chain. The study has been conducted by a Design of Experiments (DoE) approach that allows the simultaneous optimization of gradient time (t_G), column temperature (T) and binary or ternary mobile phase composition based on the retention times and peak areas of selected phenolic compounds, obtained by a restricted number of experiments. The resulting RP-HPLC methods have been used to investigate the occurrence and content of phenolic compounds in leaves and fruits of olive trees (*Olea europaea*), in monovarietal extra virgin olive oil of different cultivar and geographical origin, and in olive mill wastewater (OMWW) produced by processing the same selected batches of olive fruits by a laboratory olive oil press machine. The different phenolic compound profiles and content determined in samples differing for botanical and geographical origin and/or for the technological transformation process are illustrated and discussed.

This project has received funding by the Research Executive Agency of the European Union in the framework of MSCA-RISE Action of the H2020 Programme, Project 734899 Olive-Net.

[1] D. Corradini, F. Orsini, L. De Gara, I. Nicoletti *LC GC Europe*, **2018**, 31, 480.

A new green extraction/clean up method based on Natural Deep Eutectic Solvents (NADESs) for bisphenols and alkylphenols in foodstuffs

Lucia Croce, Carmen Palermo, Diego Centonze

Dipartimento di Scienze agrarie, degli alimenti e dell'ambiente, Università degli Studi di Foggia, via Napoli 25, Foggia, Italy

Food manufacturing comprises several production phases from the cultivation in field to the packaging. In every single step of the production the food may be unintentionally contaminated by chemical substances that are called contaminants (Cs) [1]. The Cs that have appeared only recently or that are gaining concern because of their negative effects on humans are called "Emerging Contaminants (ECs)" [2]. Bisphenols (BPs), alkylphenols (APs), some pesticides, and other substances, such as perfluoroalkyl substances (PFAS), have been classified as ECs [2]. BPs are plasticisers added to food packaging to increase its flexibility, workability, and extensibility. Bisphenol A (BPA) had been the most used BPs in packaging production until its endocrine disruptor effects was declared [3]. The European Commission, taken into account the hazard of ECs on human health, has set specific migration limits (SMLs) and maximum residue limits (MRLs) for these substances in foodstuffs. For instance, SMLs of 0.05 $mg\cdot kg^{-1}$ and 9 $mg\cdot kg^{-1}$ have been established for BPA [4] and bisphenol A diglycidyl ether (BPADGE) [5], respectively. At the moment, no limitation is reported for bisphenol AF (BPAF), bisphenol B (BPB), bisphenol E (BPE), bisphenol F (BPF) and 4-nonylphenol (4-NP) in materials and articles intended to come into contact with food. Extraction/clean-up approaches for BPs [6-9] and APs [10] in foodstuffs are typically based on conventional solid-phase extraction (SPE) or QuEChERS coupled with SPE purification steps. However, these methods require a large use of organic solvents and extensive time-consuming operations. An interesting alternative is represented by the extraction/clean-up based on deep eutectic solvents that were typically used for natural compounds (e.g. polyphenols) and Cs (e.g. PAHs) [11]. Therefore, the aim of these work was to develop a new natural deep eutectic solvent (NADES) based extraction approach for the analysis of BPs and APs (i.e. BPA, BPAF, BPB, BPE, BPF, 4-NP, BPADGE) in foodstuffs. Real samples, namely raw ham, tuna in glass jar, dried tomatoes, dried apples and dried blueberries, have been collected from the local markets. The NADESs used as extractants (polar and apolar) have been synthesized by mixing glucose with choline chloride (polar NADES), and menthol with camphor (apolar NADES) in proper ratios. The extraction/clean-up method consisted of a simple mixing of specific amounts of NADES with the homogenized real sample in a centrifuge tube and a successive treatment in a heated ultrasound system at 60°C for twenty minutes. Finally, the mixture was centrifuged and the supernatant (NADES phase) was collected, diluted and filtered before a direct analysis by HPLC-FLD. Some important variables affecting both the synthesis of NADESs and the extraction/clean-up method have been investigated. In NADES synthesis the amount of compounds and water used in the preparation, the manual mixing step in a mortar, and the synthesis conditions including stirring and heating have been studied. In the application of the extraction/clean-up method to real samples, the following aspects have been evaluated in terms of clean-up efficiency, recovery of BPs and alkylphenols, and external interferences: polar and apolar characteristics of NADES, handling of viscous NADES during operations, selection of proper lab equipments (e.g. centrifuge tubes), solvent and filter selection used for dilution and filtration. The preliminary results obtained by the proposed extraction/clean-up method based on NADESs have demonstrated that clean extracts and very good recoveries can be achieved for all the real matrices investigated.

[1] The Council of European Communities. *OJ.* **1993** L 37
[2] S. Sauvé, *Chem. Cent. J.* **2014**, 8 (1), 15.

[3] European Chemicals Agency. *https://echa.europa.eu/-/msc-unanimously-agrees-that-bisphenol-a- is-an-endocrine-disruptor* (accessed May 30, 2021).
[4] European Commission. *OJ*. **2018**.
[5] The Commission of the European Communities. **2005**, L 302/28.
[6] M Fattore et al. *Food Chem Toxicol* **2015**, 83, 68–75.
[7] G. Russo, et al. *Food Anal. Methods* **2016**, 9 (10), 2732–2740.
[8] X.-L Cao,S. Popovic. *Food Addit Contam: Part A* **2018**, 35 (1), 49–55.
[9] X.-L Cao, et al. *Food Addit Contam*: Part A **2019**, 36 (11), 1740–1747.
[10] T Czech, et al. *Sci. Total Environ.* **2016**, 557–558, 681–687.
[11] P. Makoś, et al. *Microchem. J.* **2020**, 152, 104384.

Comparison between ion chromatography and indirect photometry for the analytical determination of polyphosphates in food

Marco Iammarino[a], Aurelia Di Taranto[a], Giovanna Berardi[a], Ferdinando Benedetti[b], Sara Di Bella[b], Naceur Haouet[b]

[a] *Chemistry Department, Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata, Foggia, Italy*
[b] *Food Control Laboratory, Istituto Zooprofilattico Sperimentale dell'Umbria e delle Marche, Perugia, Italy*

Based on indirect approach, the reference method for the determination of polyphosphates (PPs) in food is characterized by high variability and possible errors in the final measurement **[1]**. This method was validated in this work, and then compared to the ion chromatography-based method, in terms of validation parameters, applicability to food analysis and management.

Regarding validation parameters, the trueness (recovery percentage) and measurement uncertainty of two methods resulted comparable, while the precision of ion chromatography approach was higher. The applicability of two methods was also investigated by analyzing commercials samples, comparing the results to the PPs indicated on the label and then obtaining results in terms of "false positive" and "false negative" responses. No "false positive" responses were obtained using the ion chromatography method, while indirect photometry gave "false positive" responses in 5% of analyzed samples. Relating to "false negative" results, this possibility was verified for all food types tested (meats, dairy products and seafood) when using indirect photometry, and only for seafood when using ion chromatography. In this regard, the percentage of "false negative" responses was equal to 23.3% and 10.0% for indirect photometry and ion chromatography, respectively (Table 1).

The comparison allowed concluding that indirect photometry is useful as "screening technique", while ion chromatography should be preferred as confirmatory technique **[2]**.

INDIRECT PHOTOMETRY

Food type	Number of analyzed samples	Number of samples with no detected PPs	PPs concentration range (as mg kg^{-1} of P_2O_5) (mean value)	N° of "false negative" responses	N° of "false positive" responses	PPs concentration range detected in "false positive" samples (as mg kg^{-1} of P_2O_5) (mean value)
Meat products	50	33	105 - 4423 (1103)	**13**	**4**	254 - 1864 (1000)
Dairy products	35	24	175 – 5139 (1728)	**4**	0	-
Seafood	35	26	113 – 722 (323)	**11**	**2**	166 - 235 (201)
Total	120	83	105 – 5139 (1099)	**28**	**6**	166 – 1864 (734)

ION CHROMATOGRAPHY

Food type	Number of analyzed samples	Number of samples with no detected PPs	PPs concentration range (as mg kg^{-1} of P_2O_5) (mean value)	N° of "false negative" responses	N° of "false positive" responses
Meat products	50	25	234.5 – 1972.2 (474.0)	**0**	**0**
Dairy products	35	20	626 – 14481.5 (4144.5)	**0**	**0**
Seafood	35	29	101.8 – 592.7 (272.8)	**12**	**0**
Total	120	74	101.8 – 14481.5 (1845.2)	**12**	**0**

Table 1 – Comparison of two analytical methods in terms of "false positive" and "false negative" responses

[1] Iammarino M., Di Taranto A. (2012). Determination of polyphosphates in products of animal origin: application of a validated ion chromatography method for commercial samples analyses. European Food Research and Technology, 235(3), 409-417.

[2] Iammarino M., Haouet N., Di Taranto A., Berardi G., Benedetti F., Di Bella S., Chiaravalle A.E. (2020). The analytical determination of polyphosphates in food: a point-to-point comparison between direct ion chromatography and indirect photometry. Food Chemistry, 325, 126937.

Stability and aging of dietary fiber from waste watermelon

Caterina Durante [a], Lisa Lancellotti [a], Laura Maletti [a,], Lorenzo Strani [a]*

[a] Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via G. Campi 103, 41125 Modena (Italy).

FAO's General-Directorate launched the International Year of Fruit and Vegetables 2021, making an official appeal to the United Nations to improve the quality and sustainability of food production, through the implementation of innovative technologies to reduce food losses and waste [1]. In this light, we attempt to offer a contribution to the knowledge in the context of the circular bioeconomy, dealing with the recovery of dietary fiber from the watermelon waste of our local productions. The fiber of the watermelon can be widely used in the food industry, as a formulation ingredient for bakery, pastry and ice cream products, as a thickener and gelling agent in industrial and artisanal preparations, etc. However, it is a material subjected to aging phenomena, or to all those irreversible transformations that modify its compositional faces and organoleptic characteristics. These results represent a stability check over time, to evaluate the resistance of these fibers to aging mechanisms.
In particular, we have evaluated the organoleptic characteristics of the fibers obtained by applying different methods of recovery and enhancement of this fraction from the pulps. Among other, we provide proximate analysis and soluble / insoluble fractions at the harvesting time, in addition to the color point and the characterization of the VOC's fraction at different aging times of the fibers themselves, by applying the SPME-GC-MS technique.
The target to be achieved with this explorative study: to evaluate the ability to resist aging processes and the shelf-life of watermelon fibers, in the total absence of other exogenous compounds such as preservatives and diastasants.

Materials and methods

Crimson watermelon pulps have been shredded and treated in different ways to obtain the fiber:
i) Centrifugation and drying in an Oven at 40°C (sample integer, as it is; CO);
ii) Centrifugation and Cryoliophilization (sample integer, CC);
iii) Washed, Centrifuged and Cryoliophilized pulps (sample WCC).
Once the preparation of the red fiber samples was completed, the color point (by UV-vis spectrophotometry) and the SPME-GC-MS analysis of the VOC's was carried out on fresh specimen (at t0 time) and after 60 days of aging (t60) in closed vials stored in the dark and in presence of std atmosphere.

Results

Among the results, the most intriguing observations have been obtained by color-point and VOC's determinations along the time. Lycopene, the main red coloring agent of these fibers, is very unstable and rapidly degrades, until the chromatic effects disappear and the whitening of the sample occurs. Similarly, the temporal evolution of the gas phase of VOC's expresses the partial instability of the solid matrix, and underlines the tendency to gradually age during the period of stock-stasis and conservation until the moment of use as an ingredient in the food formulation. Some differences have been detected. In the VOC's bouquet of the different samples and at different aging, because some species appears (i.e.: 1-methoxy-hexane for CC smpl; hexanoic acid and 2,6-nonadienal for CO one) and other deplete with time (i.e., 1-methoxy-2-propylacetate for CO smpl), assuming the role for the fiber aging. Other analytes undergo a molecular arrangement with time, such as 2,3-butanediol, present with both the cis and trans isomers at t0 but converting and stabilizing to the trans form at t60 days. This behavior could be peculiar to these fibers, but we cannot generalize yet as we have only studied one cultivar so far.

[1] FAO - Fruit and vegetables – your dietary essentials. The International Year of Fruits and Vegetables, 2021, background paper. https://doi.org/10.4060/cb2395en Rome: 2020.

Preservation and Valorization of Italian Extra Virgin Olive Oils by Rapid Evaporative Ionization Mass Spectrometry

Domenica Mangraviti[a], *Francesca Rigano*[a], *Adriana Arigó*
Paola Dugo[a,b,c,],[d] *Luigi Mondello* [a,b,c,d]

[a]*Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[b]*Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[c]*Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy;*
[d]*BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

Extra Virgin Olive Oil (EVOO) is a precious source of fats in Mediterranean diet for its nutritional and sensory properties, therefore due to its high commercial value is a primary target for fraudulent activities. European regulation established rules on the Protection Denominations of Origin (PDO) and Protected Geographical Indications (PGI) of EVOO, but still lacks of an official methodology able to assess the origin and the authenticity of the products.

Current trend proposes the use of innovative techniques to traditional methods to achieve unique fingerprinting of EVOO and build database useful for the detection of adulterations. An important role is carried out by ambient mass spectrometry (AMS) that shows unparalleled qualities within MS-based techniques. In this regard, present work aims to differentiate Italian extra virgin olive oils through the analysis of about 100 samples by an AMS approach, namely Rapid Evaporative Ionization Mass Spectrometry (REIMS). PDO and monocultivar oils belonging to different harvest years and coming from several Italian regions, were used for spectral database building and comparison beetwen top-quality oils.

REIMS approach in combination with a monopolar handpiece as sampling device was explored for the first time on liquid and poorly conductive samples. Multivariate analyses were applied to build four different chemometric models, using MS data acquired in positive or negative ionization mode for PDO and monovarietal EVOOs, and external data sets for their validation. The monocultivar oils gave positive feedback, leading to the reliable identification of each cultivar. Instead, recognition of PDO oils resulted more challenging (failure percentage $> 5\%$), probably due to the major intra-class variability, since oils labelled with the same PDO trademark often are produced blending different cultivar in different percentages.

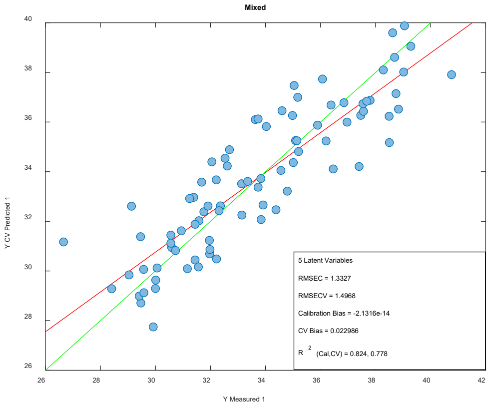
.

Prediction of *De Novo*, *Mixed* and *Preformed* fatty acids in cow milk by means of FT-NIR spectroscopy coupled with chemometrics.

Eleonora Mustorgi [a], *Cristina Malegori* [a]*, *Nicoletta Rizzi* [b], *Mattia Asti* [b], *Andrea Galli* [b]

[a] *DIFAR - Department of Pharmacy, University of Genova, Viale Cembrano 4, 16148 - Genova (GE);*
[b] *ARAL - Associazione Regionale Allevatori della Lombardia, Via Kennedy 30, 26013 - Crema (CR);*

Milk fatty acids can be classified depending on the length and unsaturation of the chain, into three categories: de novo (from C4 to C15), mixed origin (C16:0, C16:1, C17:0) and preformed (C18:0 and over). Recent studies demonstrated a correlation between the fraction of these compounds in the milk and important aspects related to feeding and health herd management [1] [2].
In this work a total of 109 cow milk samples collected from different cattle breeds fed with different feeding regimes and at different lactation stages, have been taken into account.
The first step of the analytical process consisted of lipids extraction from the raw milk samples using the International Standard Method described in ISO 15884/IDF 182 e ISO 15885/IDF 184.
The lipid fraction was analyzed in transmission mode by means of FT-NIR spectroscopy (MPA, Bruker Optics, Ettlingen, Germany) working in the spectral range between 4.000-11.000 cm^{-1}.
After non-destructive determinations, the lipid fraction has been analyzed by gas chromatography, as reference method, and the quantification of single fatty acids has been used to calculate indirectly, the amount of the three categories of interest (de novo, mixed and preformed).
Final aim of the presented work is the development of related calibration models for the prediction of the three fatty acid categories content starting from the NIR fingerprints, without the need of the chromatographic determinations.
To reach the aim, NIR spectra of the 109 samples were mathematically transformed combining two row pre-treatments, standard normal variate (SNV) and the first derivative [3], before building the calibration models using the PLS1 (partial least square) regression method. For each of the three PLS models number of latent variables, variance explained by the model, error in cross validation (RMSECV) and coefficient of determination (R^2) are determined for addressing model performances.
Results showed that the NIR spectroscopy coupled with chemometrics is a suitable tool for the global quantification of de novo, mixed and preformed fatty acids, with significantly lower errors in respect to the sum of the predictions of single fatty acid.
As an example, predicted versus measured responses for the mixed category are shown Figure 1.



[1] P. J. Moate, W. Chalupa, R. C. Boston, and I. J. Lean. *Journal of Dairy Science.* **2007,** 90 (10), 4730-4739.

[2] M. E. Woolpert, H. M. Dann, K. W. Cotanch, C. Melilli, L.E. Chase, Grant & D. M. Barbano. *Journal of dairy science*, **2016,** 99(10), 8486-8497.

[3] P. Oliveri, C. Malegori, R. Simonetti & M. Casale. A tutorial *Analytica chimica acta*, **2018**

Phthalic Acid Esters Released in Infused Drinks: Analytical Issues Related to their Determination

Ivan Notardonato[a], Alessia Iannone[a], Cristina Di Fiore[a], Giuseppe Carlucci[b], Vincenzo Ferrone[b], Mario Vincenzo Russo[a], Pasquale Avino[a]

[a] *Department of Agricultural, Environmental and Food Science (DiAAA), University of Molise, via De Sanctis, 86100, Campobasso, Italy.*

[b] *Department of Pharmacy, University of Chieti, via Dei Vestini - Campus Universitario, 66100 Chieti, Italy.*

Corresponding Author: ivan.notardonato@scuolecasacalenda.edu.it

Phthalates (phthalic acid esters, PAEs) are a group of xenobiotic substances widely used in the production of plastic due to their ability to make it softer and more workable [1]. These chemical compounds are also used in the production of containers for the consumption of food beverages, in particular hot drinks dispensed by automatic vending machines. High temperature could facilitate the migration of PAEs from the plastic container to the infused drinks [2]. This work aims at developing a simple and reproducible analytical methodology for the extraction and determination of traces of PAEs from infused drinks. The extraction methodology is based on the solid phase extraction (SPE) coupled with GC-MS for their determination. A preliminary phase is focused on the study of the most appropriate stationary phase between the C18 cartridge and Carbograph 1 by means of adsorption isotherms. The best interaction with the investigated analytes is shown by the C18 sorbent. The method development is based on the construction of breakthrough curves in order to individuate the best working conditions and on the choice of the best extraction solvent. Heptane showed the best recoveries (76.6 – 105.5 %) with a relative standard deviation < 8.3%.

For the validation of the methodology, all the analytical parameters are investigated: LODs and LOQs (respectively 0.018 – 0.120 µg mL^{-1} and 0.082 – 0.130 µg mL^{-1}), reproducibility, accuracy and precision. The overall methodology is applied to real samples such as coffee (espresso and decaffeinated espresso), ginseng coffee and tea: the results shown the presence, in low concentrations, of PAEs in infused drinks.

[1] Das M. T., Kumar S. S., Ghosh P., Shah G., Malyan S. K., Bajar S., Thakur I. S., Singh L., J. Hazard. Mater. **2021**, 409, 124496.

[2] Notardonato I., Protano C., Vitali M., Pasquale Avino, Food Anal. Methods. **2019**, 12, 2562-2571.

Authentication of PDO saffron of L'Aquila (*Crocus sativus* L.) by HPLC-DAD coupled with a discriminant multi-way approach

Alessandra Biancolillo[a], *Maria Anna Maggi*[b], *Alessandra De Martino*[c], *Federico Marini*[c], *Fabrizio Ruggieri*[a], *Angelo Antonio D'Archivio*[a]

[a] *University of L'Aquila, Via Vetoio, 67100, Coppito, L'Aquila, Italy*
[b] *Hortus Novus, Viale Aldo Moro 28 D, 67100, L'Aquila, Italy*
[c] *University of Rome "La Sapienza", Piazzale Aldo Moro 5, 00185, Rome, Italy*

One hundred and forty-nine (149) Italian saffron samples harvested in the years from 2013 to 2016 in distinct sites located in five different Italian regions (Abruzzo, Tuscany, Umbria, Campania and Sardinia) together with twenty-seven (27) commercial samples, have been analyzed by high-performance liquid chromatography with diode array detection (HPLC-DAD). Among the investigated samples, those produced in Abruzzo (L'Aquila) are particularly relevant from the quality point of view, because, since 2005, saffron of L'Aquila has been granted of the protected designation of origin (PDO) mark. In the present study, two different analytical approaches aimed at distinguishing PDO saffron of L'Aquila from the other samples have been compared. The first strategy is a more traditional approach, where the chromatograms collected at specific wavelengths are classified by Partial Least Squares Discriminant Analysis (PLS-DA). The second strategy exploits the multi-way nature of data, avoiding discarding any source of information. Consequently, the entire spectro-chromatogram is handled by N-Partial Least Squares (N-PLS) and then classified by Linear Discriminant Analysis (LDA). Both approaches provided satisfactory accuracies; the best results from the prediction point of view (estimated on an external set of samples) were achieved by the proposed multi-way methodology. In fact, this latter approach provided the most accurate results (Figure 1) and, eventually, its combination with VIP analysis led to a further improvement of predictions. This achievement indicates that three-way spectro-chromatograms contain relevant information for the characterization of the investigated samples, which is lost restricting the analysis to only few specific wavelengths.

Strategy	Total Classification rate on the test set (%)
PLS-DA on data collected at 250nm	82.8
PLS-DA on data collected at 310nm	78.6
PLS-DA on data collected at 441nm	85.7
N-PLS-LDA (spectral range *210 nm – 496 nm*)	88.6
N-PLS-LDA+VIP	94.3

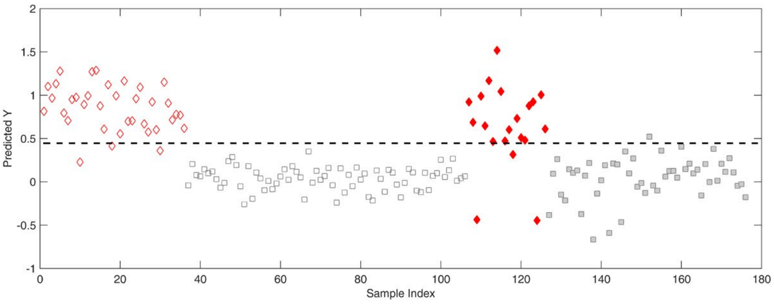


Figure 1 Total classification rates (on the test set) obtained following the diverse strategies. Y predicted vs Sample Index. Empty symbols: training samples; Filled symbols: test samples; Red Diamonds: Class PDO$_{(AQ)}$; Gray Squares: Class Non-PDO$_{(AQ)}$.

Amidation of organic acids via carbodiimide: study of the reaction in aqueous environment and its application to biological matrices

[a]*Beatrice Campanella*, [a,b] *Alessandro Fusaro*, [a]*Massimo Onor*, [a] *Emilia Bramanti*

[a] *National Research Council, Institute of Chemistry of Organometallic Compounds (CNR-ICCOM), Pisa, Italy;* [b]*University of Pisa, Department of Chemistry and Industrial Chemistry, Pisa, Italy*

Low-molecular weight organic acids (LMWOAs) are an important class of metabolites, whose alteration has been correlated with carcinogenesis and tumor presence [1]. Nonetheless, compared to other classes of biological compounds, their determination is underrepresented in bioanalytical research. The aim of this work was to develop an appropriate analytical procedure for the determination of several LMWOAs in unconventional biological matrices (i.e. cell culture medium and saliva) at sub-micromolar level.

Chemical derivatization of these metabolites is necessary to enhance the sensitivity of liquid chromatography-based determinations, especially when spectroscopic detectors are used. The coupling between organic acids and amides with carbodiimide compounds as 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) is a consolidated procedure in synthetic chemistry. However, its application in analytical determinations is likely to be jeopardized by the huge number of empirically optimized methodologies. Here, a systematic procedure based on experimental design has been used to find the best conditions for LMWOAs derivatization with 4-nitroaniline in aqueous environments, and their determination by HPLC-DAD. We found that a correct addition order of the reagents is mandatory to obtain reliable results. The method was successively applied to the analysis of LMWOAs in real matrices.

[1] S. Hori, S. Nishiumi, K. Kobayashi, M. Shinohara, Y. Hatakeyama, Y. Kotani, et al. *Lung Cancer* **2011**, 74, 284-292.

Development of a confirmatory method for the identification of mechanically separated meat (MSM) in meat products, by using inductively coupled mass spectrometry (ICP-MS) and multivariate analysis

Monica Casale[a], Marco Iammarino[b], Oto Miedico[b], Teresa D'Amore[b], Giovanna Berardi[b],

Cristina Malegori[a], Paolo Oliveri[a]

[a]*Department of Pharmacy, University of Genoa, Genoa, Italy*

[b]*Chemistry Department - Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata, Foggia, Italy*

Among different factors linked to possible adverse effects caused by meat consumption [1], in the last years, the attention of the scientific community focused on a special type of meat product: mechanically separated meat (MSM). According to EC Regulation 853/2004, MSM is referred to as "*the product obtained by removing meat from flesh-bearing bones after boning or from poultry carcasses, using mechanical means resulting in the loss or modification of the muscle fiber structure*" (European Commission, 2004).
Due to food safety concerns, the European Food Safety Authority (EFSA) asked to identify useful parameters for detecting the mechanically separated meat (MSM).
In this perspective, this study presents a new analytical approach for the identification of MSM in meat products, by using inductively coupled mass spectrometry (ICP-MS) and multivariate analysis.
One hundred meat samples (50 MSM and 50 non MSM) composed of different types of fresh meats, meat preparations and meat products were collected from local stores and then analyzed by inductively coupled mass spectrometry. Moreover, 10 'blind' commercial samples were analysed and used as an external test set in order to fully validate the model.
43 chemical parameters were analysed for each sample, so the data matrix consisted of 110 rows (samples) and 43 columns (variables).
Principal Component Analysis (PCA) was applied to the data matrix as a display method and then, in order to discriminate between MSM and non MSM products, Linear Discriminant Analysis (LDA) [2] was used as a multivariate classification technique.
LDA results were completely satisfactory, confirming ICP-MS combined with multivariate analysis as an efficient analytical approach for the identification of mechanically separated meat.

Study carried out with funding "Ricerca Finalizzata 2013" by the Ministry of Health – Project Code GR-2013-02358862.

[1] M Iammarino, R. Marino, M. Albenzio, *Int. J. Food Sci. Technol*. **2016**, 52(4), 851-863. https://doi.org/10.1111/ijfs.13350.
[2] P. Oliveri, C. Malegori, M. Casale. Chemometrics and Statistics | Multivariate Classification Techniques. *Encyclopedia of Analytical Science, 3rd edition. Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*. **2018**, 1, 481-486. doi:10.1016/b978-0-12-409547-2.14239-8

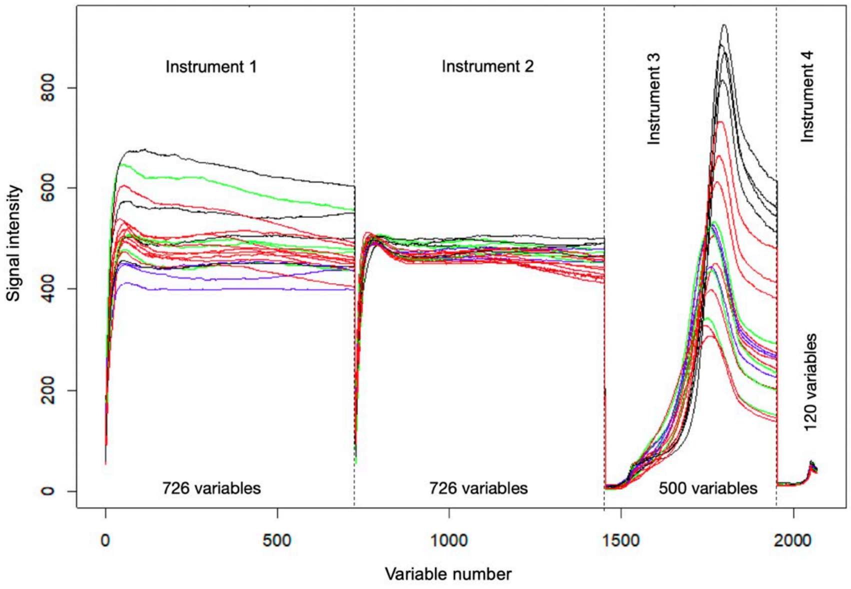
Characterization of a raw material through analytical profiles and data fusion

Emanuele Farinini[a], *Riccardo Leardi*[a]

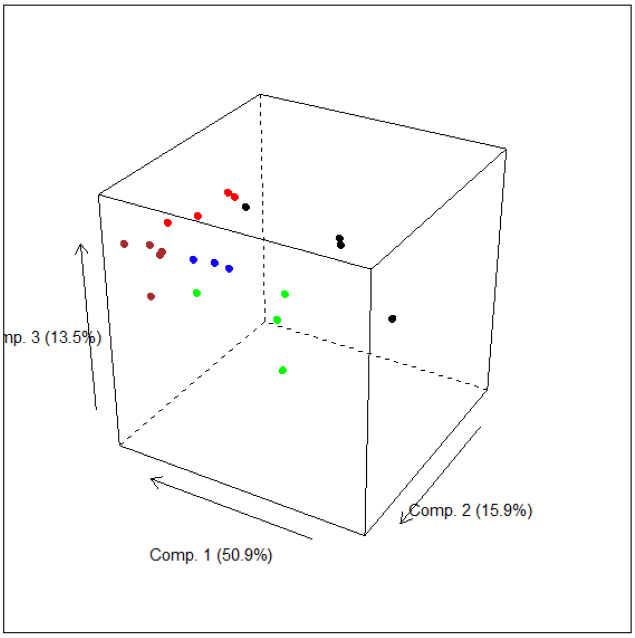
[a] *Department of Pharmacy, University of Genova, Viale Cembrano 4, I-16148 Genova, Italy.*

In several fields, particularly in the pharmaceutical and food industries, many analytical methods used for the characterization of raw materials produce profiles (i.e. calorimetry, granulometry, rheology, bioavailability etc.). From these profiles some univariate "descriptors" are usually obtained through some mathematical operations (e.g., D10, D50 and D90 in the case of Particle Size Distributions). By doing this, a huge amount of the information contained in the whole signal is lost, since the "descriptors" are not able to describe the shape of the signal. Furthermore, the "descriptors" are often not independent and therefore very much correlated, thus providing redundant information (D10, D50 and D90 are very good examples of this "matrioska effect") [1].

In the present study, four different analyses were carried out with the goal of better characterizing 20 batches of the same raw material, coming from five different suppliers.
The multivariate elaborations performed separately on the profiles obtained by each instrument have shown that all of them can sufficiently well characterize the different suppliers. However, none of them by itself was able to make each supplier fall into a specific region of the space defined by the principal components. After the application of a low-level data fusion approach, each supplier was instead well defined in the space of the three significant components, this meaning that the four analyses give complementary information.



Score Plot (80.3% of total variance)



[1] D. Copelli, A. Cavecchi, C. Merusi, and R. Leardi, "Multivariate evaluation of the effect of the particle size distribution of an Active Pharmaceutical Ingredient on the performance of a pharmaceutical drug product: a real-case study", *Chemometrics and Intelligent Laboratory Systems*, **2018**, vol. 178, pp. 1-10.

Spectroscopic Characterization and Chemometrics for the Geographical Discrimination of Italian Chickpeas

Martina Foschi [a], *Alessandra Biancolillo* [a], *Federico Marini* [b], *Francesca Di Donato* [a], *Angelo Antonio D'Archivio* [a]

[a] *Department of Physical and Chemical Sciences, University of L'Aquila, Via Vetoio 67100, Coppito, L'Aquila, Italy;* [b] *Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, Rome, 00185, Italy*

A proper untargeted characterization was carried out to attempt the geographical discrimination of three high-valued Italian chickpeas (*Cicer arietinum* L.), supplied directly by the producers and harvested in 2019 in three traditional and relatively close production areas: Navelli (Abruzzo, Central Italy), Cicerale (Campania, South Italy), and Valentano (Lazio, Central Italy). All these old landraces are protected by the Slow Food Foundation for Biodiversity and all are included in the Ark of Taste project for the safeguard of the endangered small-scale production systems belonging to the tradition of the territory. In particular, the purpose of the present study was to develop and validate a non-destructive and routine-compatible method for the geographical traceability of chickpea landraces of high traditional value as those mentioned above. In detail, the external part of 147 kernels belonging to the three varieties was analysed by Attenuated Total Reflection-Fourier Transform-Mid Infrared (ATR-FT-MIR) and FT-Near Infrared (NIR) spectroscopies. Each sample was then cut in two and the internal part of the two cross-sections was analysed by the two spectrospic methods. Spectral information was organized in four data blocks (MIRout, MIRin, NIRout, and NIRin) and single-block Partial Least Squares-Linear Discriminant Analysis (PLS-LDA) was applied. Accurate results were obtained from the single-block elaboration of both the spectroscopic profiles derived from the external part of the kernel (MIRout and NIRout), suggesting the real possibility of building a non-destructive authentication method. Nevertheless, Sequential Orthogonalize (SO)-PLS-LDA and SO-Covsel-LDA were applied on different combinations of the collected four data-blocks [1]. Although the data fusion strategies led to comparable outcomes or to a slight improvement of the already good results obtained by the single-block models, they allowed comparing the spectroscopic profiles and the two techniques employed. Eventually, VIP (Variable Importance in Projection) analysis was performed to identify the significant variables and recognize complemental information leading to a direct chemical interpretation of the classification models.

[1] A. Biancolillo, I. Måge, T. Næs, *Chemom. Intell. Lab. Syst.* **2015**, *141,* 58–67

Electroless deposition of palladium on copper: from nano to microfilms

Lorenzo Fabbri [a, b], Walter Giurlani [a], Fabio Biffoli [a], Irene Maccioni [a], Marco Bellini [e], Hamish Miller [e], Francesco Vizza [e], Massimo Innocenti [a, c, d, e]

[a] Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [b] LEM s.r.l. Socio Unico, via Leo Valiani 55, 52021 Bucine (AR), Italy ; [c] National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy; [d] Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto F.no (FI), Italy; [e] Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

Palladium plays a fundamental role in the energy field (i.e., hydrogen detection, purification, storage, and catalytic fuel cells) and in the chemical synthesis field. Palladium is also particularly popular in the electroplating industry for luxury jewellery and accessories in which is used as intermediate layer or top layer with thickness ranging from 0.2 µm to 1 µm [1]. In this work we sought to produce high quality Pd thin films with tailorable thickness onto copper substrates. To obtain a Pd layer with a very cost-effective procedure, electroless plating techniques were selected. In this work, two different types of electroless deposition techniques were used, displacement deposition and chemical deposition. In the first case a galvanic exchange reaction is exploited, while in the second one a reducing agent is used. Continuous nanometre-sized films of palladium were obtained on copper by displacement plating, their morphology was observed by optical and electron microscopy, and their thickness was measured from their EDS spectra. Metal film thickness determination by EDS spectra was made possible applying the K-ratio method [2]. In this case NIST DTSA-II software was used to simulate EDS spectra of different palladium films with known thickness using Monte Carlo approach[3]. The Pd films obtained by this procedure represent a cost-effective catalytic substrate and the process from which they derived could be easily implemented on a wide range of copper substrates (i.e., Cu-nanoparticles or Cu-nanostructures). Ammonia-based Pd chemical plating baths represent the most performant formulations to obtain palladium films in the micrometres range. To prevent copper substrates to be injured by ammonia, in this work, displacement plating of palladium was also used as a pre-treatment to make the use of these plating baths a viable way to obtain thicker palladium coatings. Palladium films showing good adherence, compact morphology under optical microscopy, and thickness over 1.5 µm (measured by XRF spectroscopy) were obtained, proofing that the combination of two different electroless techniques is the key to develop a sustainable procedure for micrometre-sized palladium coatings.

MIUR, Italy is aknowledged, with "PRIN: PROGETTI DI RICERCA DI RILEVANTE INTERESSE NAZIONALE – Bando 2017" project, protocol number 2017YH9MRK.

[1] W. Giurlani, M. Innocenti, and A. Lavacchi, "X-ray microanalysis of precious metal thin films: Thickness and composition determination," *Coatings*, vol. 8, no. 2, 2018.
[2] W. Giurlani, E. Berretti, M. Innocenti, and A. Lavacchi, "Measuring the Thickness of Metal Coatings: A Review of the Methods," *Coatings*, vol. 10, no. 12, p. 1211, Dec. 2020.
[3] W. Giurlani, E. Berretti, M. Innocenti, and A. Lavacchi, "Coating Thickness Determination Using X-ray Fluorescence Spectroscopy: Monte Carlo Simulations as an Alternative to the Use of Standards," *Coatings*, vol. 9, no. 2, p. 79, Jan. 2019.

Nucleation, growth, and morphology of deposited copper in presence of thiourea from a methanesulfonic acid-based solution

Lorenzo Fabbri [a, b], Emanuele Piciollo [b], Walter Giurlani [a], Giulia Mencherini [a], Roberta Emanuele [a, c], Antonio De Luca [a], Andrea Caneschi [c], Massimo Innocenti [a, c, d, e]

[a] Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [b] LEM s.r.l. Socio Unico, via Leo Valiani 55, 52021 Bucine (AR), Italy ; [c] National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy; [d] Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto F.no (FI), Italy; [e] Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

The need to deposit ever smaller quantities of precious metals in the field of the galvanic industry and fashion accessory necessarily passes from the possibility of depositing copper or copper alloys (bronzes) with high efficiency and improved corrosion resistance compared to past. This need is also fundamental to reduce the environmental and ecological impact for an increasingly eco-sustainable production[1]. This work is focused on the study of the role of a specific organic additive, thiourea, in the nucleation and growth mechanism of copper deposited from a methanesulfonic acid-based bath. The role of thiourea during copper nucleation and growth was verified exploiting voltametric (cyclic voltammetry) and chronoamperometric measurements in presence of three different amounts of organic additive. Chronoamperometric studies allowed to obtain information about the mechanism of nucleation and growth of the electrodeposited film. The values of current vs time were fitted to a nucleation and growth model in order to obtain different parameters and information such as type of nucleation (instantaneous or progressive), ions diffusion coefficients, nucleation rate and density of metal nuclei at the electrode surface (in this case glassy carbon electrode). The Scharifker-Hills model is the electro-crystallization model applied in this work in order to consider nucleation and growth between multiple nuclei that form simultaneously[2]. In the attempt to find a correlation between the results obtained from the Sharifker-Hills model and the progressive addition of thiourea in our alternative copper electrodeposition bath we also deposited copper in presence of the three different amounts of additive. Exploiting scanning electron microscope for surface analysis we verified that progressive nucleation is a key step in the obtainment of a shiny and homogeneous copper film and that an excess of thiourea could cause parasitic adsorption reactions on the glassy carbon surface. Applying X-ray fluorescence spectroscopy, we also verified that thiourea plays a fundamental role on the efficiency of the copper electrodeposition bath we developed.

"Regione Toscana" within the POR Creo FESR 2014–2020 "GOODGALV" Regione Toscana project is acknowledged.

2014 2020 POR CreO REGIONE TOSCANA FONDO EUROPEO DI SVILUPPO REGIONALE

Unione Europea Fondo Europeo di Sviluppo Regionale

REPUBBLICA ITALIANA

Regione Toscana

[1] W. Giurlani *et al.*, "Electroplating for Decorative Applications: Recent Trends in Research and Development," *Coatings*, vol. 8, no. 8, p. 260, Jul. 2018.

[2] B. Scharifker and G. Hills, "Theoretical and experimental studies of multiple nucleation," *Electrochim. Acta*, vol. 28, no. 7, pp. 879–889, Jul. 1983.

A new electrochemical procedure for the objective and fast evaluation of corrosion resistance

Walter Giurlani[a,b], *Tommaso Dini*[a], *Leonardo Uva*[a], *Marco Bonechi*[a], *Andrea Comparini*[a], *Antonio De Luca*[a], *Alessandra Cincinelli*[a], *Massimo Innocenti*[a,b,c,d]

[a] *Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy;* [b] *National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy;* [c] *Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy;* [d] *Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto F.no (FI), Italy;*

Noble metal coatings are commonly employed to improve corrosion resistance of metals in the electronic and jewellery industry. The corrosion resistance of electroplated goods is currently determinate with long, destructive and almost subjective interpretation corrosion tests in artificial atmosphere. In this study we present the application of electrochemical procedure to obtain fast and objective information of the antiaging coating [1].

The evaluation of precious film protection is not trivial since: (i) the use a single EIS measurement, commonly applied to organic or passivated coatings with high-impedance, does not produce reliable results. (ii) performing a simple polarization curve, to obtain the Evans diagram, is not useful due to the ideality of the noble coating. The analysed sample consisted of a bonze substrate with a gold-copper coating of various karats (from 9 kt to 24 kt) and various thicknesses (from 0.3 µm to 3 µm). The developed analysis procedure that involves repeated cycles of measurement of the open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and anodic stress, recording the current flow.

For comparison, traditional standardized salt spray test ISO 9227 was also performed. The salt spray results were evaluated by a visual inspection, differential weighing and differential colour measurement. Our findings show that the developed electrochemical procedure produces more reproducible and more objective results than traditional aging tests.

The authors acknowledge Regione Toscana POR CreO FESR 2014-2020 – azione 1.1.5 sub-azione a1 – Bando 1 "Progetti Strategici di ricerca e sviluppo" which made possible the projects "ACAL 4.0" (CUP 3553.04032020.158000165_1385), "A.M.P.E.R.E." (CUP 3553.04032020.158000223_1538), "GoodGalv" (CUP 3647.04032020.157000060) and "GIGA 4.0" (CUP 3553.04032020.158000105_1242).

[1] W. Giurlani, P. Marcantelli, F. Benelli, D. Bottacci, F. Gambinossi, M. Passaponti, A. De Luca, E. Salvietti, M. Innocenti, *Coatings* **2019**, *9*, 405.

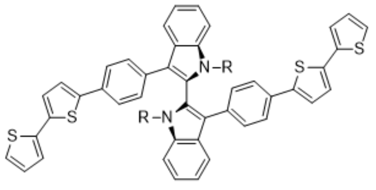
2014 2020 POR CreO REGIONE TOSCANA FONDO EUROPEO DI SVILUPPO REGIONALE
Unione Europea Fondo Europeo di Sviluppo Regionale
REPUBBLICA ITALIANA
Regione Toscana

Enantioselective electroanalysis for different chiral active pharmaceutical ingredients and a real matrix, using inherently chiral 2,2'-biindole based oligomer films.

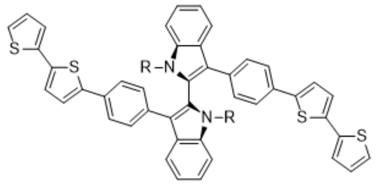
Sara Grecchi[a], *Andrea Resinelli*[a], *Serena Arnaboldi*[a], *Roberto Cirilli*[b],
Tiziana Benincori[c], *Mariangela Longhi*[a], *P. R. Mussini*[a]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133, Milan, Italy;*
[b] *Centro Nazionale per il Controllo e la Valutazione dei Farmaci, Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Roma, Italy;*
[c] *Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Via Valleggio 11, 22100 Como, Italy.*

Chirality and chiral analysis constitute a key aspect of modern chemistry and chemical technologies; the enantiomeric purity of various compounds is important in different fields, especially in the pharmaceutical one [1-3].
A systematic study case is proposed, based on a new 2,2'-biindole series **(*N*-alkyl-IND)$_2$Ph$_2$T$_4$** (alkyl= methyl, propyl or hexyl group), of easy synthesis and modulable functional properties featuring systematic variation of the *N* alkyl substituents of the pyrrolic rings in the *core* [4].



(*S*)-(*N*-alkyl-IND)$_2$Ph$_2$T$_4$



(*R*)-(*N*-alkyl-IND)$_2$Ph$_2$T$_4$

The new series shows good performances when applied as selectors in chiral voltammetry for discrimination of the enantiomers of model chiral ferrocenyl probes, either in CH_2Cl_2, by conversion into enantiopure electroactive electrode surfaces, or in achiral ionic liquid BMIMTf$_2$, as chiral additive (monomer with hexyl chains, hampering electrooligomerization). Discrimination is conveniently and reproducibly achieved in terms of significant potential differences for the two enantiomers, specularly inverting either probe or selector configuration. In one case successful discrimination is even observed with the two probe enantiomers concurrently present, either as racemate or with enantiomeric excesses, neatly accounted for by the peak current ratios [4].
Oligo-(*N*-Me-IND)$_2$Ph$_2$T$_4$ films also result in enantiomer discrimination for quite different chiral probes, active pharmaceutical ingredients: terazosin, lansoprazole, ramosetron and clopidogrel, working in aqueous buffer solution. In addition, the molecule (*S*)-clopidogrel was also tested in a real matrix, *i.e.* as the main component of the DuoPlavin®, drug in combination with acetylsalicylic acid (both active substances are antiplatelet medicines).
In all the cases, concentration calibration plots, LOD e LOQ (both on bare and modified chiral electrodes) have also been obtained, by DPV experiments.
This work confirms the wide-scope effectiveness of the new inherently chiral selectors and suggesting application to a wider pool of chiral probes of applicative interest.

[1] S. Arnaboldi, M. Magni, P. R. Mussini, *Curr. Opin. Electrochem.*, **2018**, 8, 60.
[2] S. Arnaboldi, S. Grecchi, M. Magni, P. R. Mussini, *Curr. Opin. Electrochem.*, **2018**, 7, 188.
[3] S. Arnaboldi, T. Benincori, R. Cirilli, S. Grecchi, L. Santagostini, F. Sannicolò, P. R. Mussini, *Anal. Bioanal. Chem.*, **2016**, 408 (26), 7243.
[4] L. Scapinello, S. Grecchi, S. Rossi, F. Arduini, S. Arnaboldi, A. Penoni, R. Cirilli, P. R. Mussini, T. Benincori, *Chem. Eur. J.,* **2021**, Accepted Manuscript.

Thickness determination of metal coatings by XRF without the need for certified standards.

Stefano Mauro Martinuzzi[a,b], *Claudia Giovani*[a], *Walter Giurlani*[a,e], *Roberta Emanuele*[a,e], *Elena Mariani*[a], *Stefano Caporali*[c,e], *Massimo Innocenti*[a,b,d,e]

[a] Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [b] Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto F.no (FI), Italy; [c] Department of Industrial Engineering (DIEF), University of Florence, Via di S. Marta, 3, 50139, Firenze, Italy; [d] Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy; [e] National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy

The X-ray spectrometric method is the most widespread to determine the thickness of metallic coatings in decorative electroplating applications, thanks to its ease of use, robustness, and non-destructive nature [1–3] . However, accurate measurement requires primary standards that are expensive, not always available, and must be periodically replaced due to a limited shelf-life [4,5]. Therefore, the self-production of metallic coatings with properties varying as needed represents an attractive opportunity for companies in the electroplating and metal finishing sector.
In this context, we propose a versatile and cost-effective method for determining the thickness of metallic coatings. Our method relies on a calibration curve based upon self-produced standards measured by a cross-sectional microscopy observation, either by SEM or light microscope. XRF measurements proved the excellent reproducibility of the electroplating process. The thickness distribution was also sufficiently homogeneous to meet certified standards quality requirements and quantitatively predictable using only primary current simulations, almost on simple shaped objects. Comparing different XRF quantitative methods, we demonstrated that the proposed protocol reduces costs associated with XRF instrument calibration without major drawbacks in measurement accuracy.

The authors acknowledge Center for Colloid and Surface Science (CSGI) and Regione Toscana POR CreO FESR 2014-2020 – azione 1.1.5 sub-azione a1 – Bando 1 "Progetti Strategici di ricerca e sviluppo" which made possible the projects "ACAL 4.0" (CUP 3553.04032020.158000165_1385), "A.M.P.E.R.E." (CUP 3553.04032020.158000223_1538), "GoodGalv" (CUP 3647.04032020.157000060) and "GIGA 4.0" (CUP 3553.04032020.158000105_1242).

[1] W. Giurlani, E. Berretti, M. Innocenti, A. Lavacchi, Measuring the Thickness of Metal Coatings: A Review of the Methods, Coatings. 10 (2020) 1211.

[2] R. Jenkins, X-Ray Fluorescence Spectrometry, 2nd ed., Wiley, 1999.

[3] W. Giurlani, G. Zangari, F. Gambinossi, M. Passaponti, E. Salvietti, F. Di Benedetto, S. Caporali, M. Innocenti, W. Giurlani, G. Zangari, F. Gambinossi, M. Passaponti, E. Salvietti, F. Di Benedetto, S. Caporali, M. Innocenti, Electroplating for Decorative Applications: Recent Trends in Research and Development, Coatings. 8 (2018) 260. https://doi.org/10.3390/coatings8080260.

[4] ISO 3497:2000 Metallic coatings — Measurement of coating thickness — X-ray spectrometric methods, (2000).

[5] ISO GUIDE 33:2015 Reference materials — Good practice in using reference materials, (2015).

Electrosynthesized polymers: the resorcinol case study

Stefano Mauro Martinuzzi[a,d], *Marco Bonechi*[a], *Andrea Stefani*[e], *Walter Giurlani*[a,c], *Martina Vizza*[a], *Carolina Castello*[a], *Maurizio Passaponti*[a], *Davide Vanossi*[b], *Andrea Marchetti*[f], *Claudio Fontanesi*[b] *and Massimo Innocenti*[a,c,d,g]

[a] Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; [b] Department of Engineering 'Enzo Ferrari', University of Modena and Reggio Emilia, Via Vivarelli 10, 41125 Modena, Italy; [c] National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy; [d] Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto F.no (FI), Italy; [e] Department of Physical, Computer and Mathematical Sciences, Via Giuseppe Campi, 213/a, 41125 Modena, Italy; [f] Department of Chemical and Geological Sciences, via Giuseppe Campi 103 41125 Modena, Italy; [g] Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy.

The resorcinol electrochemical oxidation is exploited for its analytical determination and is a promising method for wastewater remediation as well [1]. Indeed, it is also reported the formation of polymeric non-soluble by-products, as a result of the oxidative process, and it has to be noted that the polymerisation mechanism is still open to discussion. The resorcinol electropolymerization is a quite efficient and facile process, obtained by simple oxidation of a acid resorcinol solution, the polymerisation is triggered and a polymer film can be easily grown adherent to the electrode surface. Electrochemical phenomena are particularly complicated when they involve electroactive organic molecules, which can give rise to further reactions after being oxidised or reduced. In this case, different analytical techniques are needed to reveal the formation of reaction products and intermediates. Of course, to gain a complete understanding of the electro-polymerisation process it is essential to develop a reaction mechanism consistent with the experimental outcome. To this end, the calculation of the reaction mechanism potential energy surface, by using ab-initio quantum mechanical based methods and molecular dynamics, reveals to be a useful strategy for assessing the reaction pathway.

In this work, we propose an oxidation-polymerisation mechanism for the resorcinol molecule, which is based on the Kane-Maguire polymerization scheme. The resorcinol polymerization is considered to proceed via the dissociation of one (or two) hydrogen atom to form C-C and C-O dimers. The stability of transition states and intermediate reaction species was evaluated at the B3LYP/6-31G(d) and B3LYP/cc-pVTZ level of the theory, with also a molecular dynamics analysis (DRC algorithm). The electro-polymerisation products were determined and characterised by HPL-UV-DAD and HPLC-MS. The polymer film morphology was characterized by recording SEM micrographs. The electrochemical and adsorption-diffusion processes were studied using Cyclic Voltammetry and RDE. The proposed mechanism for the resorcinol electrochemical polymerization is fully consistent with experimental results. DFT steady-state and molecular dynamics results indicate that the base electrolyte conductive anion plays a fundamental role, making feasible the crucial first step of proton dissociation a feasible process [2].

[1] C. Wei, Q. Huang, S. Hu, H. Zhang, W. Zhang, Z. Whang, M. Zhu, P. Dai, L. Huang, *Electrochim. Acta*. **2014**, *149*, 237.

[2] M. Bonechi, M. Innocenti, D. Vanossi, C. Fontanesi, *J. Phys. Chem. A*. **2021**, *125*, 34.

Coating-free highly conductive platinum nanoparticles with efficient size-effect electrocatalytic properties

E. Mazzotta[1], *T. Di Giulio*[1], *V. Mastronardi*[2], *P. Pompa*[2], *M. Moglianetti*[2,3], *C. Malitesta*[1]

[1]*Dipartimento di Scienze e Tecnologie Biologiche e Ambientali (Di.S.Te.B.A.), Università del Salento, Italy*
[2]*Istituto Italiano di Tecnologia (IIT), Genova, Italy*
[3]*HiQ-Nano srl, Via Barsanti, 1, 73010 Arnesano, Lecce (LE)*

Over the last decades platinum nanoparticles (PtNPs) have found many increasing successful applications revealing excellent electrocatalytic activity mainly towards small molecules oxidation/reduction and oxygen reduction reaction [1], which has prompted their use in electrochemical sensing devices along with fuel cells design. Two key aspects in critically determining the beneficial exploitation of their electrocatalytic activity are the adopted synthetic scheme and the approach for their integration with the electrode surface. Concerning the first point, it is in fact well-accepted that a correct understanding of the correlation between shape/surface structure and electrochemical reactivity indispensably requires the use of clean surfaces [2]. The use of effectively surface cleaned nanoparticles freed from capping agents represents an extremely important prerequisite to subsequently evaluate their electrocatalytic properties for any reaction of interest. As to the second point, in most cases, the use of composite systems integrating organic components and PtNPs is proposed for achieving nanoparticles anchoring to the electrode surface [3]. Among materials commonly used in combination with PtNPs in the design of electrocatalytic systems are carbon-based nanomaterials as reduced graphene oxide, graphite, and carbon nanotubes, conducting polymers, and polyanionic/cationic layers.

In the present work, we report an electrocatalytic application of bare PtNPs prepared by a simple and green method [4] producing size-tunable spherical nanoparticles, without the use of catalyst-poisoning reagents and/or organic coatings. These nanoparticles are stabilized by citrate molecules which is easily and completely removed by a simple and rapid step in NaOH, allowing to obtain cleaned coating-free nanoparticles after a simple washing in water. Here we demonstrate that PtNPs can be directly anchored to the electrode surface alone without any supporting material and can be effectively used for the electrocatalytic detection of H_2O_2, which has been selected as model molecule being well known the role of platinum as electrocatalyst in its redox processes [1] and also considering the significance of H_2O_2 in biological systems. PtNPs are analyzed by X-Ray Photoelectron Spectroscopy before and after citrate removal evidencing almost complete citrate elimination as well as high nanoparticles conductivity. PtNPs are deposited by a simple drop-casting method on the electrode surface guaranteeing no aggregation and homogeneous electrode coverage, as shown by Scanning Electron Microscopy analysis. Exploiting the fine tuning of size nanoparticles afforded by the adopted synthesis method, spherical nanoparticles with size as low as 4 nm and 20 nm are prepared, as revealed by Transmission Electron Microscopy analysis, and their electrocatalytic performances towards H_2O_2 reduction are compared and discussed.

[1]S. Chen, R. Yuan, Y. Chai, F. Hu, *Microchim Acta*, **2013**, *180*, 15 – 32.

[2]M.A. Montiel, F.J. Vidal-Iglesias, V. Montiel, J. Solla-Gullón, *Current Opinion in Electrochemistry,* **2017**, *1*, 34 – 39.

[3]W. Chen, S. Cai, Q.Q. Ren, W. Wen W, Y. Zhao, *Analyst,* **2012**, *137*, 49.

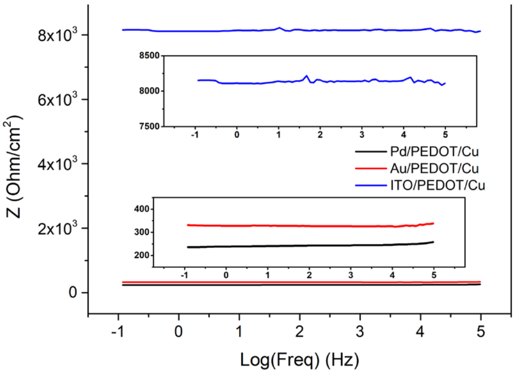
[4]M. Moglianetti, J. Solla-Gullón, P. Donati, D. Pedone, D. Debellis, T. Sibillano, R. Brescia, C. Giannini, V. Montiel, F.M. Feliu, P.P Pompa, *ACS Appl. Mater. Interfaces* **2018**, 10, *48*, 41608 – 41617.

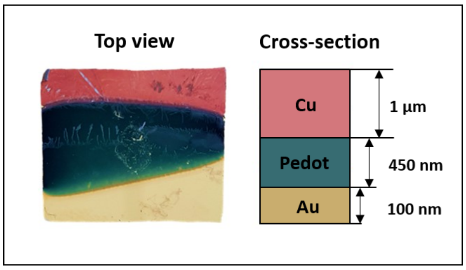
Surface analysis of a novel electro-synthesized Cu/PEDOT hybrid electronic device

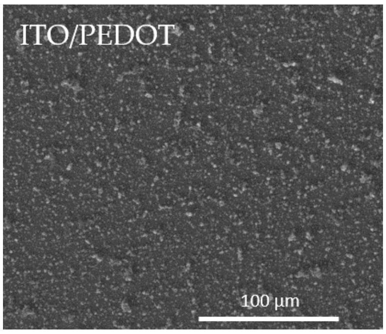
Martina Vizza [a], *Giulio Pappaianni* [a], *Andrea Stefani* [b], *Walter Giurlani* [a,c], *Enrico Berretti* [d], *Marco Bonechi* [a], *Claudio Fontanesi* [b] *e Massimo Innocenti* [a,c,d]

[a] *Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy;* [b] *Department of Engineering 'Enzo Ferrari', University of Modena and Reggio Emilia, Via Vivarelli 10, 41125 Modena, Italy,* [c] *National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze (FI), Italy,* [d] *Insititute of Chemistry of Organometallic Compounds (ICCOM) – National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy.*

Conductive polymers are nowadays attracting great attention for their peculiar mechanical and optoelectronic proprieties. In particular, poly (3,4 ethylenedioxythiophene) (PEDOT) can be used in a wide range of innovative applications, from electroluminescent devices to photovoltaics [1]. We investigated the electrochemical polymerization of PEDOT to further expand the range of possible uses of this conductive polymer. In that, electrochemically grown polymers, with respect to chemically synthesized ones, allow for the preparation of thin films in tight contact with electrode surfaces. This paves the way to the preparation of 2D layered materials to be used in spintronics or as electrodes in stacked devices [2,3]. We performed the electrochemical deposition of 3,4 ethylenedioxythiophene (EDOT) on various substrates (ITO, thin films of gold and palladium on silicon wafers), with both potentiostatic and potentiodynamic techniques. The optimal electrochemical conditions were set to obtain homogeneous PEDOT films on all the substrates. The investigation of the surface morphology and thickness of the polymer coatings on the different electrodes was performed by means of Raman, visible, ESEM, SEM and AFM characterization. These microscopic and spectroscopic techniques confirmed the high quality of the PEDOT films obtained. Then, a further layer of Copper was electrodeposited on the polymer coating on the different electrodes. In this way, a hybrid electronic solid-state device was obtained, by means of electrochemical methods only. Electrical Impedance Spectroscopy analysis confirmed the high conductivity of the PEDOT-Cu device and its ohmic behaviour over a wide range of frequencies. This further expands the possible applications of PEDOT electrochemically grown, especially to obtain systems prone to be used as electrodes in stacked devices.







[1] J. Li, J. Qin, X. Liu, M. Ren, J. Tong, N. Zheng, W. Chen, Y. Xia, *Sol. Energy* **2020**, *211*, 1102–1109.

[2] S. Mishra, A. Kumar, M. Venkatesan, L. Pigani, L. Pasquali, Fontanesi, C. *Small Methods* **2020**, *4*, 1–10.

[3] T. Nishimura, K. Tsuchiya, S. Ohsawa, K. Maeda, E. Yashima, Y. Nakamura, J. Nishimura, *J. Am. Chem. Soc.* **2004**, *126*, 11711–11717.

Study of the retention behavior of cannabinoids by reverse phase liquid chromatography (RP-HPLC)

A. Buratti[1], D. Bozza[1], S. Felletti[1], C. De Luca[1], G. Lievore[1], F. Pellati[2], V. Brighenti[2], E. Ceccon[3], S. Ongarato[3], M. Catani[1], A. Cavazzini[1]

[1] Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Ferrara 44121, Italy

[2] Department of Life Sciences, University of Modena and Reggio Emilia, Modena 41125, Italy

[3] Restek S.r.l. Via G.Miglioli 2/A – 20063 Cernusco S/N (MI)

Cannabis sativa L. is a plant that has been extensively used both medically and as a source of textile fiber for many years but is also highly debated known for its psychoactive properties **[1]**. For this reason, it has been classified as an illegal drug and the study of its chemical components and pharmacological properties has become increasingly important **[2]**. Among the natural compounds contained in *Cannabis sativa* L., currently, the number of cannabinoids identified is over 100, but their number is expected to increase further in the near future. These compounds are of great importance in the pharmaceutical field; indeed, they play a fundamental role in neurological medical conditions such as Parkinson's disease, epilepsy, and multiple sclerosis **[3]**. It is necessary to develop rapid and selective methods for their separation. In this work, a detailed study on the retention of five cannabinoids was performed. Specifically, five standards of cannabidiol (CBD), cannabigerol (CBG), cannabichromene (CBC), cannabidiolic acid (CBDA), and cannabinol (CBN) were used on a C18 column under a variety of mobile phase compositions with the purpose of understanding some features observed (such as the dependence of retention and selectivity of cannabinoids on the amount and type of organic modifier). This information is fundamental for the development of more and more efficient and fast separation methods.

References

[1] G. Skoglund, M. Nockert, B. Holst, Sci. Rep. 2013, 3, pp. 1–6.

[2] R. Mechoulam, Y. Gaoni, in: L. Zechmeister (Ed.), Fortschritte der Chemie Organischer Naturstoffe, 1967, vol. 25, pp. 175–213.

[3] K. A. Owusu, L. Saliba, A. A. Ammar, M. A. Ammar, J. Mucksavage, in: Application of Cannabinoids in Neurosciences Considerations and Implications; 2020, Crit Care Nurs Q Vol. 43, No. 2, pp. 216–231.

Adsorption of L-lysine on zeolites: effect of different framework topology and different Si/Al ratio

Mirco Cescon,[a] Tatiana Chenet,[a] Annalisa Martucci,[b] Giulia Vergine [a] Giada Beltrami [b] and Luisa Pasti[a]

[a] *Department of Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara,via Borsari 46, 44121-Ferrara, Italy*
[b] *Department of Physics and Earth Sciences, University of Ferrara, via Saragat 1, 44124-Ferrara, Italy*

The study of the ability of zeolites to adsorb amino acids is significant to improve the knowledge of the interactions between these molecules and solid surfaces. This is of fundamental importance to increase the level of understanding of much more complex systems and to select adsorbent materials able to selectively capture amino acids from aqueous solutions.[1]

Zeolites are aluminosilicate materials characterized by regular crystalline structure with microporous cavities which confer a high superficial area. The physico-chemical proprieties of zeolites depend on the composition of their framework that consist of tetrahedral units of SiO_4 and AlO_4 and, in particular, their ratio (SAR) characterizes the hydrophilic/hydrophobic behavior of the material. Moreover, the different conformation and dimension of the internal channels and cages influence the adsorption selectivity towards host molecules.[2] The ability of zeolites to adsorb biologically active biomolecules such as amino acids is of particular interest in industrial biotechnology[3] due to the fact that these adsorbent materials could be used as solid solvents to stabilize the different charged forms of the amino acids.

In this study we tested the different adsorption capacity of zeolites L and ZSM-5 towards the amino acid L-lysine. These zeolites were chosen since they present different framework, with 2D and 3D channels structures, and different pore dimensions. Moreover, for the zeolite ZSM-5, two materials having different SAR were selected to study the effect of zeolite chemical composition on the adsorption capacity. Kinetic and isothermal experiments were carried out at different L-lysine initial concentrations to study the adsorption processes. The results show high capacity towards the adsorption of L-lysine for every zeolite investigated. We found a higher capacity for zeolite L with respect to ZSM-5. Moreover, zeolite ZSM-5 with greater SAR has shown less adsorption, probably a cause of different surface charge. [1][4] Moreover, the results obtained by thermal analyses (TG-DTG-DTA) showed different interactions within the amino acid-zeolite adduct and different stability, depending on the peculiarities of the zeolites studied. Further investigation of the refinements of X ray powder diffraction patterns showed the adsorption sites, the orientation and the interactions of the amino acid molecules within the zeolite channels.

This work allowed to improve the understanding of the formation and interactions of the adducts that originate from the adsorption of amino acids on zeolites. The information obtained are useful for separation of amino acids from complex mixtures.

[1] G. Beltrami, A. Martucci, L. Pasti, T. Chenet, M. Ardit, L. Gigli, M. Cescon, E. Suard, *ChemistryOpen* **2020**, 9(10), 978–982.
[2] A. Martucci, L. Pasti, N. Marchetti, A. Cavazzini, F. Dondi, A. Alberti, *Micropor. Mesopor. Mat.* **2012**, 148(1), 174-183.
[3] K. Stückenschneider, J. Merz, and G. Schembecker, *J. Phys. Chem.* **2014**, 118, 5810-5819.
[4] T. Chenet, A. Martucci, M. Cescon, G. Vergine, G. Beltrami, L. Gigli, M. Ardit, M. Migliori, E. Catizzone, G. Giordano, L. Pasti, *Micropor. Mesopor. Mat.*, **2021**, 323, 111183.

HPLC-FTIR: a proof of concept

Carmelo Coppolino [a], Tania Salerno[b], Paola Donato[c], Luigi Mondello[a,b,d,e]

[a]*Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*
[b]*BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*
[c]*Department of Biomedical, Dental, Morphological and Functional Imaging Sciences, University of Messina, Messina, Italy*
[d]*Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*
[e]*Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy*

Fourier transform infrared spectroscopy (FTIR) is a powerful analytical tool because of its capabilities to differentiate between molecules with a very similar structure, such as isomers. For this reason, over the years great efforts have been made in development of its coupling with an HPLC system. The online HPLC hyphenation with solid deposition FTIR herein presented is possible using an evaporative interface, which not only is capable of removing the mobile phase that elutes from the column but also of depositing the analytes over a rotating ZnSe disk as a spiral track. In the meantime, IR spectra are acquired and reprocessed in order to obtain a reconstructed IR chromatogram. Moreover, if the signal to noise ratio is not sufficient for an appropriate identification, it is possible either to redeposit the sample on the same track in order to increase the spot deposited, or to rescan the track at a precise retention time of the run to increase the S/N ratio.

Two positional isomers, belonging to the furocoumarins family, angelicin and psolaren were chosen to demonstrate the discriminative power of the instrument because they show identical PDA, MS and MS/MS spectra, which do not provide discrimination. Furthermore, quantitative analysis of the same analytes were done in order to prove the linear response of the system by creating calibration curves of the two standards.

In order to improve the quality of the analysis results, other instrumental parameters can be optimized, such as disk rotation speed and disk chamber temperature, which can be reduced using LN_2. Confident compound identification and discrimination between the two isomers was achieved by library search, with QMF > 90% and limit of identification (LOI) at the sub-µg level.

Chiral analysis of Methorphan's enantiomers by HPLC coupled with FTIR

Carmelo Coppolino[a], *Tania Salerno*[b], *Paola Donato*[c], *Giampietro Frison*[d], *Luca Zamengo*[d], *Luigi Mondello*[a,b,e,f]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italia*
[b] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*
[c] *Department of Biomedical, Dental, Morphological and Functional Imaging Sciences, University of Messina, Messina, Italy*
[d] *Laboratory of Environmental Hygiene and Forensic Toxicology, DMPO Department, AULSS 3, Venice, Italy*
[e] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*
[f] *Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy*

One of the morphinan derivative, Methorphan has two enantiomers, which show different pharmacological and toxicological effects. Whereas the dextrorotary isomer Dextromethorphan (1S,9S,10S) is a safe antitussive drug available in many over-the-counter formulations and does not produce analgesic effects in therapeutic dose, the levorotatory one (1R, 9R, 10R) Levomethorphan, is a strong analgesic narcotic strictly controlled. Thus, the analytical separation and determination of these enantiomers is important for forensic, as well as for pharmacological and toxicological purposes. Online hyphenation between HPLC and solid deposition FTIR was demonstrated to be a very useful tool for separation and identification of methorphan's enantiomers. In this study, separation was achieved on a vancomycin-based column, using methanol with 0.02% of ammonium hydroxide and 0.1% of acetic acid as mobile phase, at a flow rate of 2 mL/min in isocratic conditions. The solutes were deposited, through a cyclone evaporative interface, on a ZnSe disk, which rotates at the speed of 1 mm/min. In the meantime, spectra of the analytes are acquired by the interferometer at 4 cm^{-1} resolution. The method developed is capable of providing an enantioselectivity $\alpha > 1.2$, and of carrying out the analysis in less than 15 min. Moreover, LC-FTIR results were compared with other analytical techniques such as ESI-MS, which is not able to provide sufficient information for the identification, indeed it shows only the 272 *m/z* fragment of $[M+H]^+$ in positive ionization mode.

Optimization of the Analytical Conditions for Reversed Phase Separation of Egg White Intact Proteins

Paola Donato [a], *Paola Arena* [b], *Luigi Mondello* [b,c,d]

[a] *Department of Biomedical, Dental, Morphological and Functional Imaging Sciences, University of Messina, Messina, Italy;*
[b] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[c] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*
[d] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

Protein analysis represents a current and relevant research area, due to the involvement of these macromolecules in many scientific fields, such as food/nutraceutical, pharmaceutical and toxicological sciences.
However, the most employed analytical methods for proteome characterization are based on bottom-up strategies, which aim at the characterization of proteins at the peptide level.
The analysis of intact proteins is considerably less explored than the peptides counterpart, probably due to the considerable difficulties, mainly related to matrix complexity, and the challenging development of suitable analytical methods.
Nevertheless, a growing demand for analytical procedure capable to improve routine protocols and separation performances of intact proteins has been registered.
In this research, the egg white (albumen) was selected as an election matrix for the high content in noble proteins, rich in essential amino acids; being the main constituents: ovalbumin, ovotransferrin, ovomucoid, lysozyme, G2 and G3 ovoglobulins and ovomucin.
A recently introduced BIOshell IgG 1000 A C4, 15 cm x 2.1 mm I.D., 2.7 µm stationary phase was evaluated for the analysis of the target proteins, affording high-efficiency separation even of high molecular weight components.
In detail, different analytical parameters such as the acid modifier effect, mobile phase strength, temperature, injection volume, sample dilution and memory effects were investigated in this study. Moreover, different gradient slope methods were employed to improve the resolution of closely eluting analytes.

Development of a reduced-scale fully-automated method to determine the fatty acid content in human blood by using a robotic station coupled with fast GC-MS

A. Ferracane [a], M. Galletta [a], G. Micalizzi [b], M. Zoccali [c], P.Q. Tranchida [a], L. Mondello [a,b,d,e]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*

[b] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*

[c] *Department of Mathematical and Computer Science, Physical Sciences and Earth Sciences, University of Messina, Messina, Italy;*

[d] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy;*

[e] *Department of Sciences and Technologies for Human and Environment, University Campus Bio-Medico of Rome, Rome, Italy*

This research is focused on the development of a fully automated analytical method for the trans-esterification and analysis of lipid fractions derived from a human biological sample (dried blood spot). The lipid derivatives formed - fatty acid methyl esters (FAMEs) - were then analyzed by using gas chromatography coupled with mass spectrometry (GC-MS).
Traditionally, sample derivatization procedures take a long time and involve a series of steps, and hence the use of an automatic robotic system brings advantages in terms of: the non-requirement of the presence of an operator, throughput increase, improved repeatability, and enhanced suitability for routine analysis. The proposed method is also environmentally friendly, due to a decreased reagent consumption, and to the development of a fast GC-MS method, reducing the analysis time.
Absolute quantification of 22 FAMEs was performed through calibration curve construction, using a deuterated internal standard.
Three different Standard Reference Material (SRM) samples, certified by the National Institute of Standards and Technology (NIST), were employed for accuracy evaluation.

Acknowledgements: The research was conducted within the PRIN 2017 “Cutting edge analyticals chemistry methodologies and biotools to boost precision medicine in hormone-related diseases” supported by the Ministry University and Scientific Research, Prot. 2017Y2PAB8a.

Dispersive magnetic solid-phase extraction exploiting magnetic graphene nanocomposite coupled with UHPLC-PDA for simultaneous determination of kinase inhibitors in human plasma.

Vincenzo Ferrone[a], *Marcello Locatelli*[a], *Angela Tartaglia*[a], *Pasquale Avino*[b], *Simona Bacchi*[c]
Giuseppe Carlucci[a]

[a] *Dipartimento di Farmacia, Università degli Studi "G. d'Annunzio" Chieti-Pescara, Via dei Vestini, 66100 Chieti – Italy*
[b] *Dipartimento Agricoltura, Ambiente e Alimenti, Università degli Studi del Molise, Via de Sanctis, 86100 Campobasso, - Italy*
[c] *Dipartimento Medicina Clinica, Sanità Pubblica, Scienze della Vita e dell'Ambiente, Università degli Studi dell'Aquila, Coppito, 67100 L'Aquila - Italy*

Drug analysis in biological fluids usually involves four main steps: extraction of the target substance from biological matrix, separation of interferents, detection and data handling. However, analyses in biological samples such as plasma, serum seminal plasma and urine are challenging due to the complexity of these matrices. For this purpose, several analytical techniques have been used. They include capillary electrophoresis, spectrofluorimetry, high performance liquid chromatography, and recently ultra high-performance liquid chromatography. Despite the development and the improvement of the analytical instrumentation over the last decades, sample preparation plays a key-role in the identification and measurement of the analytes. Over the last decade the development of microextraction techniques such as microextraction by packed sorbent (MEPS), solid phase microextraction, dispersive liquid-liquid microextraction (DLLME), and stir bar sorptive extraction (SBSE) have become increasingly popular for the extraction of analytes due to the high recoveries, high enrichment factors and the possibility of combining with chromatography or spectroscopy techniques. Although these techniques eliminate or reduce the volume of consumed organic solvents, they are still time-consuming processes and involves the use of toxic organic solvents (DLLME). Furthermore, MEPS and SPME involves relatively high costs, carry-over problems and batch to batch variations. Graphene (G), an emerging carbon material, has gained a lot of importance in analytical chemistry in which it has been used as sorbent in sample extraction due to its ultra-high surface area, its hydrophobicity as well as the possibility of establishing π-π interactions thanks to its delocalized electrons. However, graphene is difficult to handle, it is completely insoluble in water, it is difficult to obtain in a high yield and tends to stack to other graphene layers via π-π interactions. The possibility to combine the magnetic materials with graphene has become a research hotspot [1]. The combination of Fe3O4-graphene allows to obtain an efficient adsorbent with high adsorption capacity of graphene and separation convenience of magnetic materials.

The present study focused on the synthesis of a graphene based magnetic nanocomposite (G/Fe_3O_4) as an optimal material for MSPE and investigated its performance for adsorption of anticancer drugs in human plasma. Several parameters affecting the extraction technique such as adsorption conditions, pH of the sample solution, amount of G/Fe_3O_4, salt concentration and desorption solvent were investigated in detail. The results showed that the proposed method was easier and more sensitive compared to the existing method for the determination of kinase inhibitors.

[1] V. Ferrone, S. Todaro, M. Carlucci, A. Fontana, A. Ventrella, G. Carlucci, E. Milanetti *J. Pharm. Biomed. Anal.* **2020,** *170, 112992.*

Synthesis and characterization of polyacrylonitrile based electrospun nanofiber for the solid phase extraction of non-steroidal anti-inflammatory drugs in human plasma and their UHPLC-PDA determination

Vincenzo Ferrone, Pantaleone Bruni, Stefania Ferrari, Giuseppe Carlucci

Dipartimento di Farmacia, Università degli Studi "G. d'Annunzio" Chieti-Pescara, Via dei Vestini 66100 Chieti - Italy

Sample preparation is the most time-consuming step in the whole analytical process. It aims to enhance the selectivity, reproducibility, enrichment factor, and to bring the analytes into a solvent that is more compatible with the instrumentation. Over the past two decades, sorbent-based extraction techniques and their miniaturization have gained the attention of the scientific community, replacing liquid-liquid extraction in biological, environmental and food analyses.

Electrospinning allows the production of ultrafine materials with controlled diameter, size, morphology, and composition. Electrospun nanofibers have extraordinary attributes such as modulability in surface functionalities, high mechanical performance, high porosity and permeability, and huge chemically active surface areas.

In the field of sorbents, these characteristics allow for a high mass transfer which makes the nanofibers perfect candidates for use in solid phase extraction (SPE).

In the last ten years, micro-extraction techniques, such as stir bar sorptive extraction (SBSE), micro-extraction in solid phase (SPME), micro extraction by packed sorbent (MEPS), dispersive magnetic solid phase extraction (dMSPE) using graphene-based nanocomposites have become increasingly popular in the analysis of NSAIDs since they guarantee excellent recoveries, high enrichment factors, use of low quantities of organic solvents, reduction of extraction times and ease of operation [1].

The reported study focused on the synthesis and characterization of electrospun nanofibers as sorbents to be used in the dispersive micro solid phase extraction (d-SPE) of NSAIDs and their determination by UHPLC-PDA in human plasma. The performances of the electrospun nanofibers were investigated. Furthermore, many variables affecting the d-SPE such as the amount of adsorbent material, the adsorption time, the ionic strength, the desorption solvent, the pH of the sample, were investigated. The results show that electrospun nanofibers are very promising and performing materials to be used as sorbent. In addition, the possibility of synthesizing different kind of fibers by changing the electrospinning conditions and the polymeric precursors opens up a new scenario in the field of adsorbent materials for SPE.

[1] V. Ferrone, M. Carlucci, V. Ettorre, R. Cotellese, P. Palumbo, A. Fontana, G. Siani, G. Carlucci, *J. Pharm. Biomed. Anal*. **2018**, *161, 280.*

The importance of sorbent material selection in sampling *in vitro* and *in vivo* biologically-relevant VOCs for biomarker discovery research

Flavio A. Franchina[a,b], Delphine Zanella[b], Martina Catani[a],
Jean-François Focant[b], Luisa Pasti[a], Alberto Cavazzini[a]

[a] University of Ferrara, Dept. of Chemistry, Pharmaceutical and Agricultural Sciences, via L. Borsari 46, 44121 Ferrara, Italy; [b] University of Liège, Dept. of Chemistry, 11 Allée du Six Août, 4000 Liège, Belgium

Thermal desorption (TD) tubes are often used to trap and extract volatile organic compounds (VOC) in many fields of application, from biomonitoring to food aroma characterization [1-3]. Recently, there is a general growing interest in VOCs from biological fluids (*e.g.*, breath, serum), especially because can be considered as possible biomarkers of specific disease states.
Because of the wide variety of adsorbent materials, the tube can be filled with, it may be challenging to select the optimal tube for biological samples. Indeed, these trapping materials can be used alone or in combination and depending on the characteristics (chemical and physical), the selectivity can be tuned, as well as the sensitivity and repeatability.
In this study [4], the sampling performance of TD adsorbent materials were compared in biological samples, both in *in vitro* and *in vivo* sampling setups. Specifically, 7 different adsorbents (Tenax TA, Tenax GR, Carbopack B, 5TD, 1016, X and Sulphicarb) were used, packed singularly and in combination, on Fetal Bovine Serum (FBS) and human breath. A mix of 19 standards were employed to monitor and evaluate the sensitivity and repeatability.
Regarding the *in vitro* sampling, spiked FBS was used to mimic the biological matrix, and a dynamic headspace extraction was performed. For the *in vivo* part, breath was collected in Tedlar bags in which standards were successively flash-vaporized. In both cases, after extraction, the tubes were thermally desorbed on a comprehensive two-dimensional gas chromatography system coupled to a time-of-flight mass spectrometer (GC×GC-TOF MS).
For both sample matrices and in the targeted analysis on selected VOCs, the tubes packed with Tenax TA alone resulted the most sensitive with the highest repeatability, in the range of 2-22 RSD% for *in vivo* and 2-32 RSD% for *in vitro* sampling. Also in untargeted analysis on serum and breath, Tenax TA confirmed to be the most suitable material for sampling in terms of analyte coverage, recovery, and repeatability.

[1] Woolfenden, E. *J Chromatogr A*, **2010**, 1217, 2674-2684.
[2] Franchina, F.A.; Purcaro G.; Burklund A.; Beccaria M.; Hill J.E. *Anal Chim Acta*, **2019,** 1066, 146-153.
[3] Franchina F.A.; Zanella D.; Lazzari E.; Stefanuto P.H.; Focant J.F. *J Sep Sci*, **2020**, 43, 9-10, 1790-1799.
[4] Franchina F.A.; Zanella D.; Dejong T.; Focant J.F. *Talanta*, **2021**, 15, 222, 121569.

Qualitative screening of non-psychoactive cannabinoids in *Cannabis Sativa L.* inflorescence by linear retention index approach using hand-portable liquid chromatography

Roberta La Tella[a], *Francesca Rigano*[a], *Luigi Mondello*[a,b,c,d]

[a]*Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

[b]*Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

[c]*Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy*

[d]*BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy*

The present work reports the reliable identification of non-psychoactive cannabinoids in *Cannabis Sativa L.* inflorescence. Mass spectrometry (MS) determination after a chromatographic separation is a widespread technique in the forensic field [1, 2]. Particularly, liquid chromatography (LC) methods proved to be more suitable for their determination [3], without any need of derivatization protocols or limitation to volatile and thermostable compounds. However, the univocal identification of unknowns in LC-MS is still a complex practice, due to the lack of universal MS database related to the poor reproducibility of spectra obtained under atmospheric pressure ionization conditions, commonly employed in LC-MS. Then, the retention data is a precious information. The present research aims to build a Linear Retention Index (LRI) library of non-psychoactive cannabinoids to be used for identification purposes in real-world samples. A portable capillaryLC instrument was exploited for the analysis of *Cannabis Sativa L.* plants. Miniaturization is very interesting because offers some unique advances: short analysis time, small amount of sample, small amount of waste. A simple and fast sample preparation procedure is required, such as solid liquid extraction of a small amount of plant. At the moment, the poorly informative UV detection is employed. However, a dual-column/dual UV detector system allowed the determination of two LRI values, calculated against the homologue series of alkylarylketones, for each analyte, thus increasing the identification power: two compounds with the same LRI on the first column could be discriminated on the second one. Moreover, the ratio of the absorbances on two detectors represents a third identification criterion, thus fulfilling the recommendations of the Scientific Working Group for The Analysis of Seized Drugs.

[1] V. Brighenti, F. Pellati, M. Steinbach, D. Maran, S. Benvenuti, *J. Pharma. Biomed. Anal.* **2017**, *143*, 228-236

[2] V. Cardenia, T.G. Toschi, S. Scappini, R.C. Rubino, M.T.J. Rodriguez-Estrada, *Food Drug Anal.* **2018**, *26*, 1283-1292

[3] F. Pellati, V. Brighenti, J. Sperlea, L. Marchetti, D. Bertelli, S. Benvenuti, *Molecules*, **2018**, *23*, 2639

Aloe spp.: phenolics and anthraquinones chemical profiles in different plant extracts

M. Locatelli[a], *A. Mollica*[a], *V. Ferrone*[a], *A. Stefanucci*[a], *G. Carlucci*[a], *E. Rosato*[a], *A. Tartaglia*[a]

[(a)] *Department of Pharmacy, University of Chieti–Pescara "G. d'Annunzio", Via dei Vestini 31, Chieti 66100, Italy;*

Nature has always provided the basis for the development of new products that can be used in the treatment of human pathologies. In recent years, more and more interest has turned to natural products deriving from Aloe vera, both as food supplements and as additives in beauty products. In this study we want to provide a standardization basis of the chemical profile (phenolic compounds and anthraquinones) of the extracts of 21 different varieties of Aloe (*Aloe vera, Aloe arborescens, Aloe humilis, Aloe melanacantha, Aloe spectabilis, Aloe mitriformis, Aloe squarrosa, Aloe pelegrae, Aloe rauhii, Aloe jucunda, Aloe descoingsii, Aloe aristata, Aloe distans, Aloe concinna, Aloe morogoroensis, Aloe variegata, Aloe marlothi, Aloe ferox, Aloe dichotoma, Aloe mitriformis austera, Aloe microstigma*) in order to enhance *in-vitro* and *in-vivo* activity studies, even the lesser known varieties. The standardization took place through the analysis of the gel and cuticle extracts (separated) with HPLC-PDA methods validated both for the profile of phenolic compounds and for the profile of anthraquinones.

Generally, the total amount of phenolics is comparable between cuticle and gel, even if in some cases (*Aloe arborescens*, *rauhii*, *descoingsii*, *morogoroensis*, and *marlothi*) show higher amount in cuticle respect to the gel. In *Aloe ferox*, cuticle show lower amount respect to the gel. Compounds not reported (sinapinic acid, t-cinnamic acid and harpagoside) were not detected in all the analyzed samples. In addition, none of the phenolic compounds considered in this study were detected for *Aloe mitriformis* cuticle, *Aloe squarrosa* gel, *Aloe pelegrae* gel, *Aloe melanacantha* cuticle, *Aloe dichotoma* gel, and *Aloe mitriformis austera* gel. In *Aloe aristata* and *Aloe variegata* (both gel and cuticle) were not detected any phenolic compounds. The higher total amounts (µg/mg dry extract) of phenolics were found in *Aloe pelegrae* cuticle> *Aloe ferox* gel> *Aloe morogoroensis* cuticle> *Aloe humilis* gel> *Aloe humilis* cuticle> *Aloe rahuii* cuticle> *Aloe marlothi* cuticle> *Aloe ferox* cuticle.

The higher total amounts (µg/mg dry extract) of anthraquinones compounds were found in *Aloe vera* gel> *Aloe jucunda* cuticle> *Aloe dichotoma* cuticle> *Aloe rahuii* gel> *Aloe jucunda* gel> *Aloe spectabilis* gel> *Aloe concinna* cuticle> *Aloe arborescens* gel> *Aloe pelegrae* gel and *Aloe dichotoma* gel> *Aloe vera* cuticle and *Aloe variegata* gel> *Aloe morogoroensis* gel. None of the five anthraquinones included in the validated method were detected for *Aloe humilis* gel, *Aloe humilis* cuticle, *Aloe melanacantha* gel, *Aloe melanacantha* cuticle, *Aloe mitriformis* gel, *Aloe mitriformis* cuticle, *Aloe squarrosa* gel, *Aloe squarrosa* cuticle, *Aloe pelegrae* cuticle, *Aloe rahuii* cuticle, *Aloe descoingsii* gel, *Aloe descoingsii* cuticle, *Aloe distans* cuticle, *Aloe concinna* gel, *Aloe morogoroensis* cuticle, *Aloe marlothii* gel, *Aloe marlothii* cuticle, *Aloe ferox* gel, *Aloe ferox* cuticle, *Aloe aristata* gel, *Aloe aristata* cutformis, *Aloe mitriis* gel, *Aloe mitriformis austera* cuticle, *Aloe microstigma* gel, and *Aloe microstigma* cuticle.

This is the first study that directly compares all these varieties of Aloe from a chemical point of view and applying validated methods. This allowed to evaluate which variety (s) could be most considered for future *in-vitro* and *in-vivo* studies.

New polymeric phases for thin-film liquid phase microextraction (TF-LPME) of organic pollutants

Francesca Merlo[a], *Antonella Profumo*[a], *Clàudia Fontàs*[b], *Enriqueta Anticó*[b]

[a]*Department of Chemistry, University of Pavia, 27100 Pavia, Italy;*
[b]*Departament de Química. Universitat de Girona, 17003, Girona, Spain.*

Aim of the present study is to develop a new method based on polymeric film with plasticizer (thin-film- liquid phase microextraction, TF-LPME) for the microextraction of organic compounds belonging to three different classes of contaminants (fungicides, bactericides, and fragrances).
In the last years, green and environmentally friendly analytical strategies are increasingly required for the separation and determination of organic pollutants [1]. In this context, microextraction techniques have been successfully developed as efficient sample treatment with low consumption of organic solvent, linked to miniaturization [1], and alternatives sorptive phases have been proposed [2,3].
In this study, thin films made of a polymer (cellulose triacetate, CTA) and a plasticizer have been studied as novel sorptive phases for chlorpyrifos, triclosan and tonalide. The preparation is simple and reproducible as it only requires dipping the plasticizer into an organic dispersion containing CTA. The evaporation of the solvent leaves a continuous and homogeneous thin film, deeply characterized by different techniques (SEM, TGA, contact angle).
Therefore, six different plasticizers, namely Dibutyl sebacate (DBS), Bis(1-butylpentyl) adipate (BPA), Bis(1-ethylhexyl) sebacate (DOS), Bis(1-ethylhexyl) phalate (DOP), 2-Fluorophenyl 2-Nitrophenyl (NPOE), 2-fluorophenyl-2-nitrophenyl ether (FPNPE), with different parameters, such as dielectric constant, viscosity and chemical structure, have been investigated with the aim of selecting the most suitable membrane in terms of stability and extraction efficiency.
Preliminary tests were undertaken working with NaCl solution (100 mL, 0.01M) enriched with 100 μg L^{-1} of each analyte to study the kinetics at different extraction times (2h-8h). For each membrane composition, the amount of analyte remained in aqueous solution was determined by solid-phase-microextraction (SPME) coupled with GC-FID analysis. All analytes were quantitatively extracted after 6h with all the polymeric phases and the faster kinetic was observed with the DBS film. Subsequently, the analyte was eluted from the membranes by ultrasound assisted extraction (15 min) with 1 mL of ethyl acetate, analysed in GC-FID, without any derivatization. The extraction efficiency, kinetic behaviour and recovery highlighted that the polymeric film with DBS as plasticizer is the most performing. Therefore, this membrane has been successfully applied for pollutants microextraction in river waters and wastewaters at trace concentration (0.2-2 μg L^{-1}) afore GC-MS determination. The overall method provides quantitative recoveries, high enrichment factors, and good selectivity.

[1] K. M. Dimpe, P. N. Nomngongo, *TrAC - Trends Anal. Chem.* **2016**, 82, 199–207.
[2] R. Vera, S. Insa, C. Fontàs, E. Anticó, *Talanta* **2018**, 185, 291–298.
[3] S. H. Loh, M. M. Sanagi, W. A. W. Ibrahim, M. N. Hasan, *J. Chromatog. A* **2013**, 1302, 14-19

Acknowledgement: This research was funded by Ministerio de Ciencia, Innovación y Universidades (MCIU) through research project PID2019-107033GB-C22.

Tracing historical changes, degradation, and pollution sources of airborne polycyclic aromatic hydrocarbons (PAHs) by *Abies holophylla* and *Pinus tabuliformis* needle leaves

Zhao Wang[a], John L. Zhoud, Dongri Jin[a], Miao He[a], Donatella Nardiello[b], Donghao Li[a], Maurizio Quinto[a,b]

[a]Department of Chemistry, Yanbian University, Park Road 977, Yanji City, Jilin Province, 133002, PR China; [b]DAFNE - Department of Agriculture, Food, Natural Resources and Engineering, University of Foggia, via Napoli 25, I-71122 Foggia, Italy.

Due to their wide distribution and availability, plant leaves can be considered interesting candidates as biomonitoring substrates for the evaluation of atmospheric pollution [1]. In addition, some species can also retain historical information, for example, related to environmental pollution, due to their leaf class age [2]. In this study, the content of polycyclic aromatic hydrocarbons (PAHs) extracted from needle samples of *Abies holophylla* and *Pinus tabuliformis* by gas purge microsyringe extraction (GP-MSE) [3] in function of their class age has been investigated to obtain information regarding the degradation constant for each PAH under investigation (α values ranging from 0.173 to 1.870) and to evaluate the possibility to correlate the presence of PAHs in needles with some important pollution environmental factors. Considering air pollutant variables registered in Jilin Province, significant correlations (at 95% confidence level) have been found between coal consumption per year and anthracene contents in needles, while fluorene, phenanthrene, and anthracene resulted correlated with coal consumption. Furthermore, it has been demonstrated that the total PAH concentration in needles, for both species, increased with their age (from 804 to 3604 ng g^{-1} dry weight), showing a general tendency to accumulate these substances through years. PAH degradation rates increased instead with molecular complexity. This study could be considered a first trial to obtain historical environmental information by pine needles biomonitoring.

[1] S.-J. Kim, H. Lee, J.-H. Kwon, *STOTEN*, **2014**, *494*, 113.
[2] R. Fernández-Varela, N. Ratola, A. Alves, J.M. Amigo, *J. Environ. Manag.*, **2015**, *156*, 52.
[3] C. Yang, X. Piao, J. Qiu, X. Wang, C. Ren, D. Li, J. Chrom. A., 2011, *1218*, 1549.

A multi-analytical approach for the characterization of organic matter in agricultural soils treated with biochar

A.G. Rombolà[a], M. Montalti[a], I. Vassura[b], C. Torri[c], D. Fabbri[a]

[a] *Department of Chemistry “Giacomo Ciamician”, University of Bologna, c/o Tecnopolo di Rimini, via Dario Campana 71, 47192, Rimini, Italy*
[b] *Department of Industrial Chemistry “Toso Montanari”, University of Bologna, Campus of Rimini, via Risorgimento 4, 40136, Bologna, Italy*
[c] *Department of Chemistry “Giacomo Ciamician”, University of Bologna, via Sant’Alberto 163, 48123 Ravenna, Italy*

Biochar soil amendment continues to receive worldwide interest for integrated agricultural/environmental strategies to build soil, enhance water quality, and increase agricultural productivity, while sequestering C and thus mitigating global climate change. However, little is known about how biochar addition affects soil organic matter (SOM) composition, especially on the behavior of the active dissolved organic matter (DOM), is still unclear. DOM is a complex mixture of compounds and plays an important role in many soil ecosystem functions. Biochar amendment to soil could change SOM and DOM contents and composition, which in turn will influence overall carbon dynamics and microbial communities in soil. While several studies have compared different methods for the characterization of SOM and DOM in soil,[1] comparative studies on untreated and biochar treated soils are scant. Therefore, it is important to assess the impact of biochar amended soil applying advanced techniques to analyze the SOM and DOM in soils treated with biochar. UV-Vis spectroscopy, fluorescent excitation-emission matrices (EEMs) with parallel factor (PARAFAC) analysis for UV-fluorescence spectroscopy, analytical pyrolysis have been applied to study complex components in DOM, however, they have rarely been applied to soils with biochar.
The present study aimed to assess the effect of biochar amendment on the amount and characteristics of soil SOM and DOM in various agricultural soils treated with different types and levels of biochar Elemental analysis and analytical pyrolysis were applied for SOM characterization. DOM extraction was performed referring to method previously described.[2] After a filtration through a 0.45 μm PTFE syringe filter, the solution of DOM was obtained and stored at 4 °C until analysis. DOM samples were examined via TOC, UV-Vis, fluorescence spectroscopy and analytical pyrolysis (Py-GC-MS). EEMs, PARAFAC and cluster analysis were used to characterize the fluorescing components of DOM. The combined use of elemental analysis, fluorescence spectroscopy and analytical pyrolysis provides rigorous and detailed DOM characterization. Biochar addition to soils induced changes in SOM and DOM contents and composition depending on soil type and biochar amendment rate. The findings revealed that biochar application increased the proportion aromatic compounds of SOM and DOM. In many cases, biochar attenuated DOM leaching in soil. Moreover, the results evidence an increase in the proportion of microbial DOM in biochar amended soils. This study provides insights into the complex characteristic of soil-derived DOM in response to biochar amendment during field-scale incubations. It is therefore crucial that future research addresses the complex interactions between biochar amendment and soil C cycling, as well as how different soil types, biochars and amendment rates control these processes.

Acknowledgments: Study partly conducted within the project N. 5005053 RIFASA of the Programma di Sviluppo Rurale (PSR 2014-2020) della Regione Emilia Romagna Tipo operazione 16.1.01. We owe our special thanks to "Ganazzoli Filippo" farm where the experimental trial was conducted.

[1] E. C. Minor, M. M. Swenson, B. M. Mattson, A. R. Oyler, *Environ. Sci-Proc. Imp.* **2014**, 16 (9), 2064-2079.
[2] M. Ghidotti, D. Fabbri, O. Mašek, C. L. Mackay, M. Montalti, A. Hornung, *Environ. Sci. Technol.* **2017**; 51, 6580-6589.

Impact of REE enriched soil in *Vitis vinifera L.* plant

Marcella Barbera[a,b]*, Pierpaolo Zuddas*[b]*, Eristanna Palazzolo*[a]*, Filippo Saiano*[a*]

[a] *Dipartimento SAAF, Università degli Studi di Palermo, Viale delle Scienze ed.4, 90128, Palermo, Italy*
[b] *Sorbonne Universitè, METIS, 4 Place Jussieu, 75005, Paris, France*

The extensive use of Rare Earth Elements (REE) in new applications is constantly rising, consequently, waste releasing of REE in subsoils and groundwater is emerging very fast. It is thus critical for both users and researcher to understand the potential impact of anthropogenic soil pollution from REE in agricultural and food products. Although there is increasing environmental concern regarding these elements, the mechanisms behind REE differential uptake and tolerance by *Vitis* vinifera L. are still poorly investigated. We report herein experimentation in which we investigate the REE transfer from a poor soil and an REE artificially enriched soil in REE to Vitis vinifera L. organs (Roots, Xylem-sap, leaves). We wondered if Vitis vinifera L. organs put in place specific mechanism in REE transfer in function of the environmental condition of growth. Our semi-natural experimentation reports evidence of REE different behaviour between plants organs even if the soil enrichment does not influence significatively the ∑REE accumulation in Vitis vinifera L. suggesting that Vitis vinifera L. roots limit the accumulation of all REE group in aerial part, and thus in grapevine products, determining a natural control of REE polluted soil.

M. Barbera et al., *Chemosphere* **2021**, *266*, 128993.

Removal of poly- and perfluoroalkyl substances (PFAS) from aqueous matrix by using hydrogel containing nanostructured carbon material

C. Stevanin[a], R. Boaretto[a], T. Chenet[a], M. Cescon[a], S. Caramori[a], L. Pasti[a]

[a] Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L.Borsari 46, 44121 Ferrara, Italy

Extensive use of per- and polyfluoroalkyl substances (PFAS) has caused their ubiquitous presence in natural waters. Consequently, water remediation from “forever chemicals” is a critical issue that needs to be addressed promptly due to their adverse health outcomes in humans. It is therefore necessary to study new methods for the removal and elimination of pollutants from water, and membrane-based technology has rapidly become a competitive alternative with respect to traditional methods [1]. In particular, mixed matrix membranes (MMMs), that are composed by a continuous polymer phase and a dispersed inorganic filler have gained importance due to their fouling, permeate quality and longevity characteristics. Different types of fillers had been utilized in MMMs, such as zeolites, mesoporous silica, carbon nanotubes (CNTs), montmorillonite, and metal–organic frameworks.

In this work nanostructured carbon material has been included in several formulations of hydrogels which differ in hydrophilicity, cross-linking and swelling, and the adsorption efficiency of all the formulations had been determined and compared to the adsorption of powder nanostructured carbon. The hydrogel matrices were obtained using two different monomers of polyethylene glycol diglycidyl ether (PEGDE): PEGDE_Ethyl, that presents hydrophilic characteristics, and PEGDE_Propyl, which is more hydrophobic; these two PEGDE monomers were used in a mass polymerization reaction with other two different monomers having amine substituent groups, JEFFAMINE and polyethylene glycol amine functionalized, which give different types of cross-linking in the membranes; for each formulation, a percentage of carbon material, 2.5% and 5% w/w, was added.

For all MMMs, adsorption kinetic and isotherm studies were carried out using the batch method, where a known quantity of adsorbent was placed in contact with a known volume of solution with a known concentration of PFAS. All the results obtained were compared with the values obtained for the powder of the carbon material. Kinetic studies showed that within 6 hours the kinetic equilibrium is reached for all the MMMs considered, while the swelling study was carried out by weight control at different contact times up to 24 hours. The isothermal study was carried out with a contact time of 24 hours, keeping the solution stirred at room temperature and evaluating, by LC/MS analysis, the change in concentration of the pollutant in the solution before and after the contact with the adsorbent material.

The data obtained showed that the MMMs has a higher adsorption efficiency than the powdered nanostructured carbon material. Furthermore, the different hydrophilicity, swelling and cross-linking characteristics play a fundamental role in the saturation capacity (qs) of different MMMs. In fact, qs was improved of about 20 mg of PFAS per gram of adsorbent material, passing from qs = 30.1 ± 1.4 mg / g for powdered nanostructure carbon material to values higher than 50 mg/g for MMMs. Moreover, the results showed that the MMM with the highest saturation capacity was the membrane with higher hydrophobicity characteristics which presents more affinity for per- and polyfluoroalkyl substances.

[1] A.E. Amooghin et al., *Progress in Materials Science*, **2019**, *102*, 222-295

New eco-sustainable feed in aquaculture: determination of potentially toxic elements in relation to the inclusion of *Hermetia illucens* raised on omega-3-enriched substrates

C. Truzzi[a]*, S. Illuminati*[a]*, F. Girolametti*[a]*, I. Olivotto*[a]*, M. Zarantoniello*[a]*, P. Riolo*[b]*, S. Ruschioni*[b]*,*
A. Annibaldi[a]

[a]*Department of Life and Environmental Sciences, Università Politecnica delle Marche, Via Brecce Bianche, 60131 Ancona, Italy;*

[b]*Department of Agricultural, Food and Environmental Sciences, Università Politecnica delle Marche, via Brecce Bianche, 60131 Ancona, Italy*

This study is part of the research project NUTRIFISH (Fondazione Cariverona, code n. 2017.0571), aimed at studying the possibility of including the Diptera *Hermetia illucens* (HI), (fed on coffee roasted by-product enriched with microalgae/polyunsaturated fatty acids) as aquafeed ingredient. According to the concept of circular economy, insects represent good candidates as aquafeed ingredients, and many studies have recently been published about their inclusion in fish feed [1, 2]. Nevertheless, there are some potential safety risks linked with insect consumption. HI prepupae can accumulate Cd, Pb, and Hg from rearing substrates, even if the risk of exposure to potentially toxic elements (PTEs) is relatively low and in compliance with European Union regulations [3]. In this study we investigated the presence of Cd, Pb, Ni, As, Hg in larvae (20 days), juveniles (2 months) and adults (6 months) of *Danio rerio*, used as experimental model, reared on five experimental diets characterized by increasing inclusion levels (0, 25, 50, 75 and 100% respect to fish meal) of full-fat HI prepupae meal. Quantitative determinations of Cd, Pb, Ni, and As were made with an Agilent DUO 240FS atomic absorption spectrometer (Agilent, Santa Clara, CA 95051, USA) equipped with a graphite furnace (GTA120 Graphite Tube Atomizer) and a Zeeman-effect background corrector. The total mercury content was quantified by thermal decomposition amalgamation atomic absorption spectrometry using a Direct Mercury Analyzer (DMA-1, Milestone, BG, Italy) [3].

The PTEs content of HI-enriched diets was lower (Pb ~0.50, As ~0.14, Ni ~0.44 mg kg^{-1} dw) or of the same order (Cd ~0.49, Hg ~0.039 mg kg^{-1} dw), with respect to the control diet based on fish meal. All diets showed a PTEs content lower than the legal limit referred to undesirable substances in animal feed (2002/32/EC), except for Ni for which no legal limit was reported.

In *Danio rerio*, PTEs content (min-max, mg kg^{-1} dw) of larvae, juveniles, and adults was, respectively: Cd, 0.044-0.054, 0.32-0.74, 0.35-0.79; Pb, 0.26-0.67, 0.23-1.19, 0.17-1.18; As, 0.38-0.50, 0.11-0.67, 0.10-0.88; Hg, 0.006-0.012, 0.075-0.082, 0.095-0.109; Ni, 0.52-3.3, 1.2-4.7, 1.7-6.9.

Our results demonstrated that the content of PTEs in *Danio rerio* can be influenced both by the type of diet administered and by the life stage of the animal itself. In particular, by increasing the HI meal dietary content, we observed in the specimens at the same life stage, an increase of the content of Cd, Pb and Ni, and a reduction in the content of As, while the concentration of Hg remained almost constant. Considering the PTEs content in relation to the life stage, there is generally an increase in the content of Cd, Pb, Hg and Ni from larvae to juvenile, while the shift of *Danio rerio* from juvenile to adult involved a significant increase in the content of Hg and Ni. Larvae typically have a reduced ability to bioaccumulate metals such as Pb and Ni compared to juveniles and adults, and are unable to bioaccumulate Hg, which is bioaccumulated in later life stages.

[1] M. Zarantoniello, B. Randazzo et al. *Scientific Reports.* **2020**, *10*, 10648N.
[2] J.A. Vargas-Abúndez, B. Randazzo et al. *Aquaculture*. **2019**, *498*, 1-11.
[3] C. Truzzi, A. Annibaldi et al. *Int J Environ Res Public Health.* **2020**, *17*, 2121

Inter-annual variability of size-segregated particulate mercury in the aerosol over Terra Nova Bay, Antarctica

Flavio Vagnoni [a], Federico Girolametti [a], Matteo Fanelli [a], Giada Giglione[a], Annamaria Falgiani[a,b], Anna Annibaldi [a], Cristina Truzzi [a], Silvia Illuminati [a]

[a] Department of Life and Environmental Sciences, Università Politecnica delle marche, Via Brecce Bianche, 60131 Ancona, Italy;
[b] ARPA Marche, Department of Ascoli Piceno, Via della Repubblica 34, 63100 Ascoli Piceno, Italy

Mercury (Hg) is a persistent pollutant of global concern due to its volatility, mobility, persistence, and strong tendency to bioaccumulate in food chains. The Hg cycle has unique features in polar regions with respect to the lower-latitude areas with particulate mercury (PHg) playing a key role in the global mercury biogeochemical cycle [1].

Within the framework of the Italian National Program for Antarctic Research (PNRA), size-segregated size-fractionated PHg measurements were carried out at Faraglione Camp, ~3 km far from the Italian station "Mario Zucchelli" (Terra Nova Bay, Antarctica), during three summer seasons, from 2017 to 2020. Samples were collected every 10 days by a six-stage high-volume cascade impactor with size classes between 10 µm and 0.49 µm.

The average PHg concentrations in PM10 was 65 ± 5 pg m^{-3} with a range of 22–135 pg m^{-3}. These results were comparable to those recorded in the same sampling site and in other Antarctic areas. They also confirmed the surprisingly high concentrations of PHg characterizing the continent with respect to those measured in urban and industrialized areas. The trimodal aerosol mass distribution reveals that more than half of the total PHg came in the size > 1.0 µm. Hg in the two coarse fractions was probably produced by the adsorption of oxidized Hg species transported by air masses from the Antarctic plateau or produced locally by sea ice edges. PHg in accumulation mode seemed to be related to gas–particle partitioning with sea salt aerosol.

Our study provided important information for assessing the size distribution of particulate mercury in Antarctica and enhanced the general understanding of the Hg cycle in remote areas. The better comprehension of the particulate mercury distribution and formation mechanisms will lead to improved global transport and deposition models and could help refine pollution-control strategies around the world.

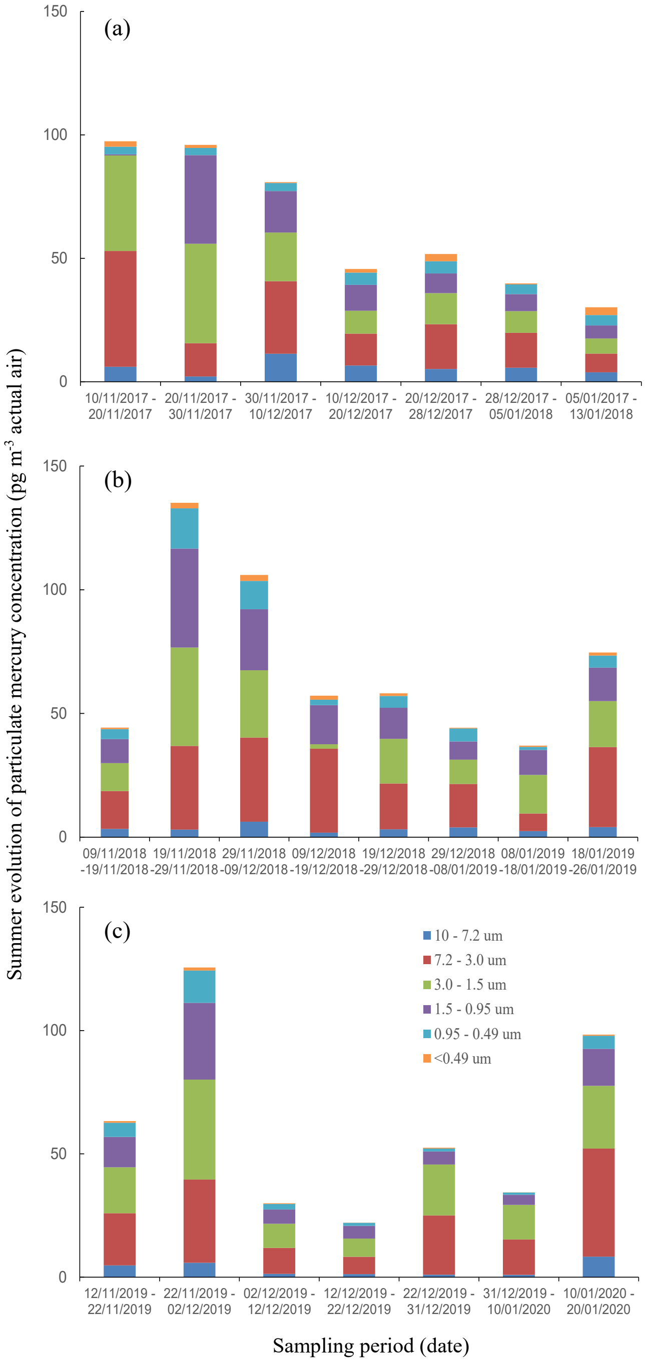


Figure 1. Size distribution of PHg during austral summers (a) 2017-18, (b) 2018-19 and (c) 2019-20.

[1] Dommergue, A.; Sprovieri, F.; Pirrone, N.; Ebinghaus, R.; Brooks, S.; Courteaud, J.; Ferrari, C.P. *Atmos. Chem. Phys.*, **2010**, *10*, 3309–3319.

Analysis on organic residues from Hellenistic and Roman pottery in ancient Taormina: the contexts from the domus in Villa San Pancrazio

Anna Irto [a], Giuseppe Micalizzi [b], Clemente Bretti [a], Mariano Morganti [c], Marta Venuti [c], Lorenzo Campagna [c], Concetta De Stefano [a], Luigi Mondello [b,d], Paola Cardiano [a]

[a] Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali CHIBIOFARAM, Università degli Studi di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina; [b] Chromaleont s.r.l., c/o Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali CHIBIOFARAM, Università degli Studi di Messina, Viale Palatucci, Polo Universitario Annunziata, 98168 Messina, Italia; [c] Dipartimento di Civiltà Antiche e Moderne DICAM, Università degli Studi di Messina, Polo Universitario dell'Annunziata, 98168 Messina; [d] Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali CHIBIOFARAM, Università degli Studi di Messina, Viale Palatucci, Polo Universitario Annunziata, 98168 Messina, Italia.

Organic residue analysis is an analytical approach that can address a wide range of archaeological questions regarding diet, food storage and processing, ritual and medical practices, trade and use of commodities, domestication of animals, thus providing important clues on the daily life of ancient societies. Organic residues can be generally found in pottery as visible solidified sediments inside containers, as charred surface deposits or, more commonly, as absorbed residues within the vessel wall. It is in fact well established that burial or entrapment within the ceramic matrix preserves organic compounds from chemical and biological degradation, thus allowing, in some cases, their identification after many centuries [1]. So far, several efforts have been carried out for the effective recovery, detection and quantification of specific compounds and their degradation products in archaeological materials. Accordingly, the identification of the so-called "archaeological biomarkers", i.e. compounds that can be used as tracers of past human activities and that cover a variety of organic compounds such as lipids, proteins, carbohydrates, is of crucial importance. Since lipids are the most durable and widely occurring biomarkers in the archaeological record, the development of analytical protocols for the determination and quantification of specific biomarkers, related to the use or the processing of animal or plant fats, beeswax, plant leaf waxes, resins, recovered from archaeological sites, has been considerably spreading along the scientific community [2]. Although proper analytical techniques have been successfully employed to unravel archaeological questions and to identify specific components, some issues remain open. For instance, very few is reported on the investigation of alternative sample treatment strategies, including green approaches, or about the study of the soil matrices, where pottery has been recovered [3]. In this sense, this contribution is focused on the preliminary results of the organic residues analysis performed on samples collected inside Hellenistic and Roman Imperial pottery and soils found during archaeological research currently ongoing in the ancient houses within Villa San Pancrazio in Taormina (ME). The excavations in the area had already provided several archaeological deposits related to domestic activities with sets of well-preserved vessels, characterized in many cases by traces of their contents. These deposits have been excavated by adopting rigorous collection protocols aimed at the conservation of this kind of traces avoiding contamination. These are therefore particularly favourable contexts for the development of the aforementioned analysis program. Preliminary lipids analyses in term of fatty acids have been carried out by using GC techniques. Focusing on total fatty acid composition, a derivatization step was performed for converting lipid compounds into more volatile and less polar fatty acid methyl esters (FAMEs) derivatives.

[1] R.P. Evershed, *Archaeometry* **2008**, 50, 895-924.
[2] J. Kałużna-Czaplińska, A. Rosiak, M. Kwapińska, W. Kwapiński, *Crit. Rev. Anal. Chem.* **2016**, 67-81.
[3] C. Heron, R.P. Evershed, L.J. Goad, *J. Archaeol. Sci.* **1991**, 18 (6), 641-659.

In-situ dual-enzyme digestion of proteinaceous pictorial binders

Elena C.L. Rigante [a], *Cosima D. Calvano* [b,c,d], *Tommaso R.I. Cataldi* [a,c], *and Luigia Sabbatini* [a,c,d]

[a] *Dipartimento di Chimica, Università Degli Studi di Bari Aldo Moro, Via Orabona 4, 70126, Bari, Italy;*
[b] *Dipartimento di Farmacia-Scienze Del Farmaco, Università Degli Studi di Bari Aldo Moro, Via Orabona 4, 70126, Bari, Italy;*
[c] *Centro Interdipartimentale SMART, Università Degli Studi di Bari Aldo Moro, Via Orabona 4, 70126, Bari, Italy;*
[d] *Centro Interdipartimentale "Laboratorio di ricerca per la Diagnostica Dei Beni Culturali", Università Degli Studi di Bari Aldo Moro, Via Orabona 4, 70126, Bari, Italy.*

The identification of organic binders in works of art is a key element to correctly describe the artist's preferences, to explore the painting framework, and, most importantly, to choose the best conservation and restoration practices. Protein-based pictorial binders, such as animal glue, egg or milk, had been broadly employed in cultural heritage until the XVI century [1]; their recognition by non-invasive analytical approaches is highly demanded. Proteomic approaches based on mass spectrometry (MS) have become increasingly popular for protein binder's identification in works of art. Some quasi- or non-invasive (*in situ*) approaches have been proposed to investigate painting layer composition while respecting the artwork's integrity and preciousness [2]–[6].

With the main aim of improving the identification of egg proteins, which are not easily digested by trypsin, in this communication we describe the extension of a previous *in situ* method [4], [7]. A very small piece of poly (2-hydroxyethyl methacrylate)/poly (vinylpyrrolidone) hydrophilic gel (3 mm×3 mm) is immersed in a dual-enzyme solution (trypsin:chymotrypsin, 1:1, v:v) and then applied on the painting surface where the *in situ* protein digestion occurs. The piece of gel is later moved into an extraction solution to collect the peptide mixture.

Optical microscope images and spectrophotocolorimetry spectra confirmed that neither damage nor colour alteration of the painting layer occurred, and no hydrogel residue was left. This protocol was first tested on fresh and aged painting layer standards and later applied to a painted altarpiece "Assumption of the Virgin" and on some statues of the Nativity scene both dating back to the XVI century and preserved in Altamura's Cathedral (Apulia, Italy). Both MALDI-ToF-MS and reversed-liquid chromatography via electrospray ionization (ESI) coupled to a linear ion trap MS analysis allowed to disclose the aminoacidic sequences of peptides and, therefore, the identity of the sampled proteins. The combined activity of trypsin and chymotrypsin was particularly successful in enhancing protein digestion, thus increasing protein coverages for all the common employed binders including egg, milk and glue.

[1] L. Campanella *et al.*, *Chimica per l'arte*, **2007**, Zanichelli.

[2] E. Barberis *et al.*, *Microchem. J.* **2018**, 139, 450–457.

[3] G. Ntasi *et al.*, *J. Proteom*. **2020**, 231, 104039.

[4] C. D. Calvano *et al.*, *Talanta*, **2020**, 215, 120882.

[5] P. Cicatiello *et al.*, *Anal. Chem.* **2018**, 90, 10128–10133.

[6] P. G. Righetti *et al.*, *J. Proteome Res.* **2020**, 19, 2914-2925.

[7] C. D. Calvano *et al.*, *Anal. Chem.* **2020**, 92, 10257–10261.

A volatolomic approach for the characterization of essential oils from aromatic plants by GC/MS

G. Spadaccino[a], L. Frabboni[a], F. Petruzzi[b], G. Disciglio[a], A. Mentana[b], D. Nardiello[a], M. Quinto[a,c]

[a]DAFNE - Department of Agriculture, Food, Natural resources, and Engineering - Università degli Studi di Foggia, Via Napoli, 25 - 71122 Foggia (Italy), [b]Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata, Via Manfredonia 20, Foggia 71121, Italy, [c]Department of Chemistry - Yanbian University, Park Road 977, 133002 Yanji, Jilin Province (China)

In this study a volatolomic approach is proposed for the characterization of the volatile organic compound (VOC) composition of essential oils (EOs) extracted from common aromatic plants. Five species (*Prunus spinosa* L., *Salvia officinalis* L., *Eucalyptus globulus* L., *Melissa officinalis* L. and *Mentha x piperita* L.), particularly widespread in Southern Italy, were selected as recognized sources of natural bioactive compounds with beneficial properties [1,2].

Hydro distillation and solid-liquid extraction with ethanol at different percentages were used to obtain EOs, and their extraction capabilities were compared analyzing chromatographic profiles obtained by headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography - mass spectrometry (GC-MS). The analytical procedure was optimized in term of SPME fiber, adsorption time and desorption time. GC-MS analyses were performed allowing the profiling of the VOC fingerprint in each plant extract [3]. Experimental data were processed by a statistical multivariate approach (Analysis of Variance and Principal Component Analysis obtained for compounds and chemical classes), confirming that EO aroma profiles were statistically different for each of the selected five plants. The proposed volatolomic approach has proved to be an easy and efficient tool to study the aroma profile, allowing the collection of specific information and opening new perspectives and opportunities for the detection and identification of VOCs in agricultural and ecological applications.

[1] S. Tariq, S. Wani, W. Rasool, K. Shafi, M.A. Bhat, A. Prabhakar, A.H. Shalla, M.A. Rather, *Microbial Pathogenesis*. **2019**, *134*, 103580.
[2] M. Vergine, F. Nicolì, C. Negro, A. Luvisi, E. Nutricati, R. Annunziata Accogli, E. Sabella, A. Miceli, *Rec.Nat.Prod.* **2019**, *13*, 205.
[3] G. Spadaccino, L. Frabboni, F. Petruzzi, G. Disciglio, A. Mentana, D. Nardiello, M. Quinto, *J. Pharm. Biomed. Anal.* **2021**, *202*, 114167.

Determination of matrine-based biopesticides, a new class of emerging contaminants, in vegetable extracts by Liquid Chromatography/Tandem Mass Spectrometry

D. Nardiello[a], W.M.V. Marchesiello[a], S. Sportelli[b], L. Bonassisa[b], M. Quinto[a,c]

[a]DAFNE - Department of Agriculture, Food, Natural resources, and Engineering - Università degli Studi di Foggia, Via Napoli, 25 - 71122 Foggia (Italy); [b]BonassisaLab srl- s.s 16 Km. 684.300, Zona Industriale ASI, Incoronata – 71122 Foggia (Italy); [c] Department of Chemistry - Yanbian University, Park Road 977, 133002 Yanji, Jilin Province (China)

In recent years, botanical pesticides have been added to the class of plant fungicides, widely used in modern agriculture to guarantee productivity and quality [1]. Matrine is a well-known alkaloid, used in traditional Chinese medicine to treat cancer, and cardiac and skin diseases [2]. Moreover, as a bioactive component against various insect pests, pathogenic fungi, and bacteria, the matrine extracts from the family *Sophora* plants are also applied as biopesticides on fruits and vegetables [3]. Nevertheless, the use of matrine and its derivate oxymatrine can cause hazards to food safety and human health, since in overdose amounts, these highly polar basic compounds may have negative effects on the respiratory and renal systems. Being the inclusion of new compounds in the European-database pesticides a long process, in Europe, matrine-like alkaloids are still not authorized pesticides (Reg. EC No. 396/2005), and sensitive and reliable analytical methods are required for their determination at trace levels.

In this work, a high-performance LC/tandem MS method is described for the quantitative analysis of matrine and oxymatrine in fruits and vegetables. The sample preparation process has been optimized considering different extraction solvent mixtures and clean-up procedures, obtaining satisfactory recoveries, in accordance with the European directives. Finally, the method has been validated evaluating linearity, selectivity, detection and quantification limits, precision, and accuracy, and it has been successfully applied to the to the analysis of vegetable origin food samples.

[1]. X. Liu, Y. Tian, F. Dong, J. Xu, Y. Li, X. Liang, Y. Wang, Y. Zheng, *J. AOAC Int.* **2014**, *97*, 218.

[2]. V. Oveissi, M. Ram, R. Bahramsoltani, F. Ebrahimi, R. Rahimi, R. Naseri, T. Belwal, H.P. Devkota, Z. Abbasabadi, M.H. Farzaei, *DARU J. Pharm. Sci.* **2019**, *27*, 389.

[3]. L. Sabatino, M. Scarangella, F. Lazzaro, M. Scordino, G. Picariello, C. Leotta, P. Traulo, G. Gagliano, *J. Environ. Sci. Health - Part B Pestic. Food Contam. Agric. Wastes.* **2015**, *50*, 862.

Volatolomics study of X-ray irradiated dairy products by HS-SPME/GC-MS

Carmen Palermo[a], *Annalisa Mentana*[b], *Rosalia Zianni*[b], *Lucia Croce*[a], *Diego Centonze*[a]

[a] *Dipartimento di Scienze Agrarie, degli Alimenti e dell'Ambiente, Università degli Studi di Foggia, via Napoli 25, Foggia, Italy*
[b] *Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata, via Manfredonia 20, Foggia, Italy;*

The increasing demand for raw and fresh dairy products, such as soft cheese, with desired organoleptic characteristics and health benefits, requires alternative technologies for inactivation of pathogenic microorganisms in particular of Listeria monocytogenes [1, 2]. In a report of the European Commission [3] and in a recent review [4], the use of food irradiation in half a century of studies is well summarized highlighting the potential benefits of this preservation technique. In Europe, the general application of X-rays to dairy products has been limited to one cheese (Camembert) [5-7], but the irradiation processing of raw and fresh dairy products is of great interest to the food industry. However, irradiation treatments may cause possible biochemical changes in lipid and protein profiles that can affect the quality and safety of products [1].

For these reasons, the purpose of this work was to study the volatile organic compounds (VOC) in X-ray irradiated soft cheeses. A volatolomics approach based on headspace solid-phase microextraction (HS-SPME) combined with gas chromatography-mass spectrometry (GC-MS) was developed to evaluate the irradiation effects on the volatile profile of soft cheeses, as a function of different radiation treatment parameters. Five different SPME fibres, namely polyacrylate (PA), polydimethylsiloxane (PDMS) carboxen/polydimethylsiloxane (CAR/PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB) and divinylbenzene /carboxen/polydimethylsiloxane (DVB/CAR/PDMS), were tested in terms of number and relative amount of compounds extracted. Moreover, temperature and extraction time were evaluated for the HS-SPME process efficiency. The volatile compounds of 0, 1.5 and 3 kGy irradiated samples were extracted by the selected SPME fibre and analyzed by the optimized method. VOCs, identified by means the linear retention index and by MS data obtained from NIST library, were analyzed by a multivariate statistical approach in order to investigate the generation of off-odors and flavors induced by X-ray irradiation and to understand the quality and maintenance of the nutritional and sensorial values. Volatile compounds belonging to chemical classes of acids, alcohols, aldehydes, esters, and miscellaneous were identified in all the experimental samples and interesting variations were noted among them as a function of the irradiation dose.

[1] O.B. Odueke, et al., *Food and Bioprocess Technology* **2016**, 9 (5), 751-767.
[2] V. Lacivita, et al., *LWT*, **2019**, 103, 186-191.
[3] European Commission Report, Brussels, 25.11.2016 COM, **2016**, 738, 1-22.
[4] P. B. Roberts, *Radiation Physics and Chemistry*, **2014**, 105, 78-82.
[5] Stefanova R., et al., *Food Analytical Methods*, **2010**, 3, 225-252.
[6] European Law, *Official Journal of the European Union*, Document 52009XC1124(02), No. 283/**2009** C 283,5.
[7] Chauhan S.K. et al., *Comprehensive Reviews in Food Science and Food Safety*, **2008**, 8 (1), 4-16.

Fast separation of free fatty acids using reversed-phase and weak anion-exchange mixed-mode stationary phase and ultra-high performance liquid chromatography-high resolution mass spectrometry

Nicolò Riboni[a], *Monica Mattarozzi*[a], *Monica Maffini*[a], *Simona Scarpella*[b], *Federica Bianchi*[a], *Maria Careri*[a]

[a] *University of Parma, Department of Chemistry, Life Sciences and Environmental Sustainability, Parco Area delle Scienze 17/A, Parma, Italy;* [b] *Waters SPA, Viale T. Edison 110, 20099 Sesto San Giovanni, Milan, Italy*

Fatty acids (FAs) have a strong influence on health, well-being and disease risk, being included in a large number of biological functions, e.g. being energy sources and membrane constituents and regulating the production of bioactive mediators [1]. Based on the chain length, FAs have been classified as medium-chain (8-13 C atoms), long-chain (14-20 C atoms) and very long-chain (more than 21 C atoms). Common long-chain and very long-chain unsaturated FAs, such as essential FAs, are also classified as omega-3 (e.g. eicosapentaenoic, docosapentaenoic and docosahexaenoic acids), omega-6 (e.g. linoleic and arachidonic acids), omega-7 (e.g. palmitoleic and vaccenic acids) and omega-9 (e.g., oleic and erucic acids), according to the location of the first double bond from the last carbon [2]. Due to their amphiphilic properties, containing both hydrophobic hydrocarbon chains and hydrophilic head groups, their separation represents an analytical challenge.

In the present study, two commercial stationary phases, i.e. CSH C_{18} and Atlantis PREMIER BEH C_{18} AX [3], were tested for the separation of a complex mixture of 21 FAs, encompassing saturated medium-, long- and very long chain FAs, unsaturated long and very long chain FAs, cis/trans isomers, and isomers of odd- and branched-chain FAs. The analysis was performed using ultra-high-performance liquid chromatography coupled with high resolution mass spectrometry (UHPLC-HRMS). The role of different parameters, including surface area, type of mixed mode stationary phase and effect of mobile phase pH were investigated in order to provide an insight on the mixed-mode separation mechanism and the retention of FAs. BEH C_{18} AX, owing to the higher surface area and the anion-exchange capacity up to pH 8.5, proved to be more versatile offering superior retention of FAs. The UHPLC system allows shortening analysis time within 5 min without the need for derivatization or ion-pairing reagents. The Synapt G2-Si HDMS QTOF operating in scanning MS^E mode enabled the simultaneous acquisition of both low energy and high energy spectra for the univocal identification of detected compounds. Finally, the UHPLC-HRMS method using the BEH C_{18} AX column was successfully applied to the separation and unambiguous identification of FAs of nutritional interest in a dietary supplement sample.

[1] P.C. Calder*, J. Parent. Enteral Nutr.* **2015**, 39, 18S.
[2] FAO/WHO: *Fats and oils in human nutrition: report of a joint expert consultation*. FAO Food and Nutrition Paper 57. Rome, FAO, **1994**.
[3] K.R. Smith, P. Rainville, *Waters Corporation Application Note*, 720 0 06747EN, **2020**.

Exploring new preparation and analytical applications of carbon nanomaterials and quantum dots from rice husk

Andrea Speltini [a,b], *Petra Bianchini* [a], *Francesca Merlo* [a], *Federica Maraschi* [a], *Lorenzo Malavasi* [a], *Antonella Profumo* [a]

[a] *Department of Chemistry, University of Pavia, via Taramelli 12, 27100 Pavia;*
[b] *Department of Drug Sciences, University of Pavia, via Taramelli 12, 27100 Pavia.*

Rice husk (RH) is a non-food biomass produced in hundreds of tons every year in Lombardy, which has a relevant rice industry as well as other Italian regions, e.g. Piedmont and Veneto. Millions of tons of RH are generated each year worldwide and presently no cost-effective and large-scale re-uses of RH have been achieved; indeed RH is a waste - hardly compostable due to the high silica content - that is reduced to ash before being disposed of [1].

In this work, RH was chosen as precursor to obtain carbon nanomaterials, including carbon quantum dots (CQDs), to be used as potential solid-phase extraction (SPE) sorbents for pharmaceuticals in natural waters.

The materials preparation starting from RH ashes (from pyrolysis, 700°C, 2 h, N_2 flow) was explored revising and improving a literature method based on sequential acidic oxidation by H_2SO_4 and HNO_3 followed by hydrothermal treatment (HT) [1]. By controlling the ultrasound-assisted oxidation steps (2 × 2 h, 2 × 4 h, 2 × 10 h), it was possible modulate the morphology and size of the carbon nanomaterials. These consisted of a fraction collected by 0.22 µm filtration and composed of nanoparticle (20-30 nm) aggregates of 2-5 µm, and a finer suspension of CQDs collected in the filtrate solution. For instance, the CQDs prepared by 2 × 2 h and 4 × 4 h oxidations showed a decrease of the final size from about 10-12 nm to about 5-7 nm. As a remarkable advantage, satisfactory results were achieved by one-pot oxidation in sulfonitric mixture (8 h, ultrasounds), prior to HT, with no significant difference in terms of size and shape in the obtained products. Explorative dispersive SPE tests were carried out on the materials collected by filtration in tap water samples (5 mL, native pH and pH 2.5) enriched with 5 µg/mL of Cefuroxime (CEF), Ciprofloxacin (CIP) and Dexamethasone (DEXA) as probe xenobiotics representative of water emerging contaminants. All compounds are quantitatively adsorbed from water, both at native and acidic pH, evidencing a good sorption affinity for these compounds with different physical-chemical properties. Eluates with methanol, acidic methanol (5% v/v formic acid) and alkaline methanol (5% v/v ammonia) under vortex or ultrasounds, were analyzed by HPLC-UV. The best findings were observed on the nanomaterial prepared by one-pot oxidation, on samples at pH 2.5, using acidic methanol for the elution, obtaining quantitative recovery for CEF and DEXA (91-110%, RSD ~10%), while the fluoroquinolone antimicrobial is more retained under these conditions (recovery < 45%). Based on these preliminary results, investigations are now continuing for their determination at environment-significant concentrations. Additionally, CQDs, which are arousing great interest in many research areas as a new class of zero-dimensional, quasi-spherical carbon nanostructures, are exploited for their peculiar sorption properties [2]. Experiments are ongoing to immobilize the dots onto proper substrates to be used for dispersive SPE of the target probes.

[1] Z. Whang, J. Liu, W. Wang, Z. Wei, F. Wang, P. Gong, J. Wang, N. Li, B. Liu, Z. Zhang, W. Wang, L. Sun *J. Mater. Chem. B* **2017**, *5*, 4679.
[2] J. Chen, Z. Gong, W. Tang, K.H. Row, H. Qiu *Trend. Anal. Chem.* **2021**, *134*, 116135.

Pomegranate, bud-derivatives, and lavender: three example of eco-sustainable industrial supply chains

Federica Turrini[a], *Dario Donno*[b], *Gabriele Beccaro*[b], *Paola Zunin*[a], *Raffaella Boggia*[a]

[a] *Department of Pharmacy, University of Genoa, Viale Cembrano 4, 16148 Genoa, Italy;*
[b] *Department of Agriculture, Forestry and Food Science, University of Torino, Largo Braccini 2, 10095 Grugliasco (TO), Italy;*

The development of sustainable solutions for the management of agricultural and food waste is currently one of the main challenges of our society. In developing countries, agriculture and food processing generate large amounts of waste and by-products, with a significant environmental, economic, and social impact. On the other hand, many of these products could represent a potential source of valuable compounds (i.e., bioactive compounds, macronutrients, micronutrients, and dietary fibers)[1].

Pomegranate (*Punica granatum*) crop is nowadays spread all over the world for its high longevity, drought and salinity resistance and adaptability to different climatic conditions. Pomegranate juice is the main industrial product obtained from this fruit, and the by-products of this processing represent an expensive disposal problem but also a promising source of bioactive compounds to be exploited. Particularly, ellagic acid (EA), in its free form or in the form of ellagitannins (ETs), is considered the main phenolic compound responsible for the numerous health properties of pomegranate and is mainly concentrated in the by-products with respect to the juice (both external peels and internal edible marcs)[2].

Bud-derivatives and lavender represent two supply chains studied in the Finnover "Innovative strategies for the development of cross border green supply chains" project, namely a cross-border Italy/France EU Interreg Alcotra project (2017-2021). The aims of this research project were the innovation and the sustainable implementation of several agro-industrial processing chains in view of the green circular economy and the valorization of the biodiversity of the Alcotra territory. In particular, the management of waste deriving from agricultural and food processing is one of the main topics of the project. Bud-derivatives, which represent a relatively new category of plant food supplements obtained macerating meristematic tissues of trees and plants (i.e., buds and young sprouts), are very expensive products compared to other botanicals, since the collection period of their raw materials is extremely limited over time[3]. Lavender essential oil has been widely used as herbal medicine for centuries in the traditional medicine. The solid by-products remaining after the distillation of lavender, are considered as a potential and still under-utilized source of phenolic compounds to be valorized.

In this study, the innovative and eco-compatible Pulsed Ultrasound-Assisted Extraction (PUAE) demonstrated to be a promising strategy to valorize these waste and by-products by obtaining in a very short time (10-20 min), using only food-grade extraction solvents, new potential ingredients to use in different fields (food, cosmetic, pharmaceutical etc.).

[1] C. Torres-León, N. Ramírez-Guzman, L. Londoño-Hernandez, G.A. Martinez-Medina, R. Díaz-Herrera, V. Navarro-Macias, O.B. Alvarez-Pérez, B. Picazo, M. Villarreal-Vázquez, J. Ascacio-Valdes, C.N. Aguilar, *Front. Sustain. Food Syst.* **2018**, *2*, 52.

[2] F. Turrini, R. Boggia, D. Donno, B. Parodi, G. Beccaro, S. Baldassari, M.G. Signorello, S. Catena, S. Alfei, P. Zunin, *Eur Food Res Technol* **2020**, *246*, 273-285.

[3] F. Turrini, D. Donno, G.L. Beccaro, P. Zunin, A.M. Pittaluga, R. Boggia, *Foods*, **2019**, 8, 466.

Development and validation of a fast GC method for the quantification of free amino acids in biological samples

Federica Vento[a,b], Danilo Donnarumma[b], Emanuela Trovato[b], Giuseppe Micalizzi[b], Luigi Mondello[a,b,c,d]

[a]Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy

[b]Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy

[c]BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, Italy

[d]Unit of Food Science and Nutrition, Department of Medicine, University Campus Bio-Medico of Rome, Rome, Italy

Metabolomics aims at the quantitative analysis of all metabolites in a given biological system. Amino acids (AAs) are important targets for metabolic profiling since, besides being the basic structural units of proteins, possess also several other functions. They are a source of energy, neurotransmitters, precursors of hormons, porphyrins and polyamines. Elevated amino acid levels in blood plasma and urine are well-known markers for inborn metabolic disorders, such as phenylalanine in phenylketonuria or branched-chain amino acids in maple syrup urine disease. Amino acids also serve as markers for nutritional influences, e.g., urinary taurine levels are an indicator for fish intake, while the 1-methylhistidine level in urine correlates with meat protein intake. Due to the important biological functions of amino acids, fast and reproducible analytical methods are needed for their quantitative analysis. In this work, we validated a fast-gas chromatography/mass spectrometry (Fast-GC/MS) method for the quantification of a free amino acid (FAAs) by using a rapid derivatization procedure (2 min at room temperature) to convert the polar FAAs into more volatile, GC-amenable species. We employed propyl chloroformate as derivatizing agent, since allowed us to perform the derivatization directly in aqueous solution. As for the chromatographic approach, the use of a GC separation, rather than a liquid chromatography (LC) method allowed to exploit the benefit of an entirely automatic identification process, thanks to the coupling with electron ionization MS (EI-MS) detection. Furthermore, GC, compared to LC, is characterized by a higher retention data reproducibility, mainly due to the negligible influence of the mobile phase, so that retention data in the form of the well-established Linear Retention Index (LRI) parameters can be combined to MS data in a dual-filter database to achieve univocal and highly reliable identification in a fully automatic way [1]. The samples were directly derivatized and analyzed with a custom made column (10 m × 0.25 mm × 0.25 µm). For the detection, a single quadrupole mass spectrometer was used. Pure standard compounds underwent the same sample preparation protocol and were used for method validation purposes (LOD, LOQ, precision, linearity and accuracy were determined) and to build a database including both mass spectra and LRIs of each AA derivative, providing a reliable identification in the real samples. Quantitative determination of FAAs was also carried out on plasma and urine samples.

[1] G. Micalizzi *et al*, *Anal. Bioanal. Chem.* **2020**, *412*, 2327.

Analysis of carbazole alkaloids in *Murraya Koenigii* by means of HPLC-MS/MS with combined acquisition modes

[a]*Eduardo Viteritti,* [a]*Eleonora Oliva,* [a]*Federico Fanti,* [a]*Sara Palmieri,* [a]*Fabiola Eugelio,* [a]*Alessia Pepe,* [a]*Manuel Sergi,* [a]*Dario Compagnone*

[a]*University of Teramo, Faculty of Bioscience and Technology for Food, Agriculture and Environment, Teramo, Italy.*

Carbazole alkaloids are a class of tricyclic hetero-aromatic alkaloids, with two benzene rings fused onto a pyrrole ring structure, but it is still difficult to gain a full classification of those compounds. A large number of carbazole alkaloids has been isolated from Rutaceae family, and in particular, the genus *Murraya* represents the richest source of carbazole alkaloids [1]. Several studies have also shown the antimicrobial and anti-inflammatory effects of carbazole alkaloids from vegetable origin [2]. The wide range of bioactive compounds present in *Murraya Koenigii* made the study of this plant interesting both from a biological point of view, but also an analytical challenge. Recently, the structures of all isolated compounds from *Murraya Koenigii* were mainly examined by means of high performance liquid chromatography (HPLC) coupled to different types of detectors, such as UV/VIS, photodiode array detector (DAD) and mass spectrometry (MS) [3]. These structures were mainly detected by means high resolution MS (HRMS [2]). Generally, the analysis is performed in targeted mode, either by means of triple quadrupole (QqQ), or in untargeted mode through quadrupole time-of-flight (Q-ToF). The aim of this work is the characterization of the bioactive compounds belonging to the class of carbazole alkaloids present in the leaves of this plant by means of HPLC connected in series to a hybrid triple quadrupole linear ion trap mass spectrometer. A sensitive method was developed for the simultaneous determination of three target analytes, while other compounds not included in the target list, were detected by using predictive multi experiment approach coupling multiple reaction monitoring (MRM), information-dependent acquisition (IDA) and enhanced product ion scan (EPI). Competitive Fragmentation Modeling-ID (CFM-ID) was used to predict MS/MS spectra from the chemical structures of the compounds. The obtained MRM transitions were used as survey experiment; the IDA method then was used to trigger the EPI scans by analyzing MRM signals. Dependent MS/MS spectra acquired in EPI mode for target and unknown compounds were confirmed by matching them with MS/MS spectra found in literature. Furthermore, an efficient extraction and clean-up procedure was used in order to obtain good recoveries of all analytes (from 60% to 85%) by solid-phase extraction (SPE), providing also low matrix effect. In this study, for target analytes (Mahanimbine, Koenimbine, Koenigicine) the evaluation of LOQ (MRM) and LOD (IDA-EPI) were performed. The obtained results demonstrated that the MRM-IDA-EPI method can simultaneously provide quantitative information for the target analytes and a putative identification for many compounds belonging to different classes of carbazole compounds, even if not previously detected.

[1] Huang, L., Feng, Z. L., Wang, Y. T., & Lin, L. G. (2017). Anticancer carbazole alkaloids and coumarins from Clausena plants: A review. *Chinese Journal of Natural Medicines*, *15*(12), 881–888. https://doi.org/10.1016/S1875-5364(18)30003-7

[2] Joshi, T., Mahar, R., Singh, S. K., Srivastava, P., Shukla, S. K., Mishra, D. K., Bhatta, R. S., & Kanojiya, S. (2015). Quantitative Analysis of Bioactive Carbazole Alkaloids in Murraya koenigii. *Natural Product Communications*, *10*(2), 293–295. https://doi.org/10.1177/1934578x1501000220

[3] Nalli, Y., Khajuria, V., Gupta, S., Arora, P., Riyaz-Ul-Hassan, S., Ahmed, Z., & Ali, A. (2016). Four new carbazole alkaloids from Murraya koenigii that display anti-inflammatory and anti-microbial activities. *Organic and Biomolecular Chemistry*, *14*(12), 3322–3332. https://doi.org/10.1039/c6ob00267f

Potentiometric investigation of solution equilibria in the Sn^{2+}-H_2O-F^- system using pH, Fluoride Ion-Selective and Sn(Hg) amalgam electrodes

Mariacristina Bianco [a*], *Ermanno Vasca* [a]

[a] *Dep. Chemistry and Biology "A. Zambelli", University of Salerno, Via Giovanni Paolo II, 132 Fisciano (SA), Italy*
[*] *m.bianco16@studenti.unisa.it*

Solution equilibria of tin in the +2 oxidation state are very difficult to study, owing to the relatively easy oxidation of the element to Sn(IV).

The behaviour of tin(II) in aqueous solution is characterized by a strong acid hydrolysis, widely studied through specific techniques, including potentiometry. [1-2-3] Although most of the authors agree on the speciation model, depending on the experimental concentration of tin(II), the numerical values of the stability constants seem not consistent.

The available data have so far been interpreted assuming the existence of mononuclear species $SnOH^+$, $Sn(OH)_2$ and $Sn(OH)_3^-$ at low concentrations of tin(II) (< 0.5 μM), while, at higher metal concentrations polynuclear species predominate, probably one or more among $Sn_2(OH)_2^{2+}$, $Sn_2(OH)_3^+$ and $Sn_3(OH)_4^{2+}$. [4]

Of considerable importance are the species that Sn(II) forms with halides, and in particular, binary complexes with fluoride, SnF_2, widely used in the cosmetic industry and specifically, in toothpaste formulations as a source of fluoride, whose adsorption on dental enamel is favoured by the presence of Sn^{2+} ions. [5]

Ternary species formed by Sn^{2+} with hydroxide and some halides, Br^- and Cl^- have also been reported, while, up to now, studies concerning the formation of mixed ternary species Sn^{2+}, OH^-, F^- are absent. [6-7]

In this work the study of the formation equilibria of mixed Sn^{2+}-OH^--F^- complexes by potentiometric titrations of hydrolysed tin solutions with NaF solutions, monitoring $[H^+]$, $[Sn^{2+}]$ and $[F^-]$, simultaneously, using glass membrane electrode (GE), tin amalgam electrode and fluoride ion-selective electrode (ISEF), respectively, is reported. The formation of the different complexes is also investigated by NMR techniques.

[1] F. Séby, M. Potin-Gautier, E. Giffaut, O. F. X. Donard, *Geochim. Cosmochim. Acta*, **2001**, 65, 3041–3053

[2] R. S. Tobias, *Acta Chem. Scand.,* **1958**, 12, 198–223

[3] F. Salvatore, D. Ferri, M. Trifuoggi, C. Manfredi, E. Vasca, *Ann. Chim.*, Rome, **1997**, 87, 477–481

[4] R. M. Cigala, F. Crea, C. De Stefano, G. Lando, D. Milea, S. Sammartano, *Geochim. Cosmochim. Acta*, **2012**, 87, 1-20

[5] D. W. Bartlett, B. G. Smith, R. F. Wilson, *Br. Dent. J.*, **1994**, 176(9), 346-348

[6] C. E. Vanderzee, *J. Am. Chem. Soc.*, **1952**, 74(19), 4806-4808

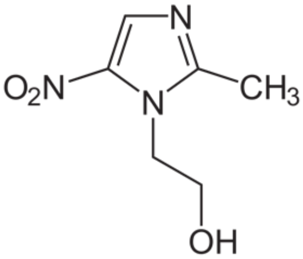
[7] C. E. Vanderzee, D. E. Rhodes, *J. Am. Chem. Soc.*, **1952**, 74(14), 3552-3555

Study on acid-base properties of metronidazole and on interaction with As^{3+} in aqueous solution

Federica Carnamucio, Massimiliano Cordaro, Claudia Foti, Ottavia Giuffrè

Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina, Viale F. Stagno D'Alcontres,31, 98166, Messina.

Metronidazole (MTZ), belongs to the nitroimidazole family, is used like antibacterial and anti-inflammatory antibiotic. The presence of traces of this pharmaceutically active compound in wastewater is a threat to human health and environment [1]. For this reason, the knowledge of the acid-base properties of MTZ and of its interactions with metal cations of environmental interest is crucial.
The determination of protonation constants of the ligand and formation constants of the metal-ligand species was achieved by potentiometric analysis in aqueous NaCl solution at three different ionic strength values (0.15, 0.5, 1 mol L^{-1}) and temperature (15, 25, 37°C). Based on potentiometric results, very simple speciation models are proposed, which include only ML species for the As^{3+}-MTZ system.
^{1}H-NMR titrations were also employed on MTZ and As^{3+}-MTZ solutions at $t = 25$°C and $I = 0.15$ mol L^{-1} in order to confirm protonation and formation constants obtained by potentiometry.
Enthalpy change values, both for protonation and for complex species were obtained by the dependence of the constants on the temperature. The dependence of protonation and formation constants on the ionic strength was also determined in the range $0.15 \leq I$ / mol $L^{-1} \leq 1$ and $t = 25$°C.
The sequestering ability of MTZ towards As^{3+} was evaluated in different conditions of pH, ionic strength and temperature by an empirical parameter known as $pL_{0.5}$, *i.e.* ligand concentration able to bind 50% of the trace metal cation [2].



Metronidazole (2-Methyl-5-nitroimidazole-1-ethanol, MTZ)

[1] J.O. Eniola, R. Kumar, M.A. Barakat, *Environ. Sci. Pollut. Res.*, **2019**, *26*, 34775-34788.
[2] A. Gianguzza, O. Giuffrè, D. Piazzese, S. Sammartano, *Coord. Chem. Rev.*, **2012**, *256*, 222-239.

A new approach in the critical evaluation of the hydrolysis constant of the Zn^{2+} cation

Gabriele LANDO, Rosalia Maria CIGALA, Demetrio MILEA, Francesco CREA

Università degli Studi di Messina, Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, CHIBIOFARAM, V.le F. Stagno d'Alcontres, 31, 98166 Messina, Italy

In the evaluation of solution equilibria involving a metal cation, the knowledge of its hydrolysis constants is mandatory. This means that they must be known in the same medium, temperature and ionic strength of the system under analysis. In the literature, great attention has been paid to this aspect and many papers and compilation were published [1-3]. In this contribution, the original data reported in the literature for the zinc hydrolysis constants have been critically re-analyzed according to two approaches: 1) analyzing conditional values in different ionic media; 2) using the so called "Pure water model" [4], *i.e.*, transforming the data into a general non-interacting ionic medium to be used in combination to all the weak species that can be formed in a solution. The first approach is used as reference method, the second assumes that equilibrium constants are influenced by the formation of weak species formed between the reactants and the ions of the supporting electrolyte. The correcting equation, based on the solution of the mass balance equation, is:

$$\log K' = \log K - \log (1 + K^{\mathrm{ZnX}} \cdot [\mathrm{X}] \qquad (1)$$

Where K' is the apparent formation constant in the presence of the competing ion "X", which forms the weak species "ZnX" of K^{ZnX} stability, log K is the corrected (to pure water) stability constant. The output of this work consists of several sets of parameters for the ionic strength and temperature dependence, related to eq. (2), for zinc hydrolysis constants valid in various ionic media (i.e., conditional hydrolysis constants) and one set of parameters for the "pure water model" to be used in any ionic medium in combination to all the weak species formed in solution.

$$\log K_{I,T} = \log K_{\mathrm{I,T}}^{0,\theta} - z^* \cdot 0.51 \cdot \mathrm{D.H.} + \mathrm{C}\cdot I + \mathrm{F}_1(T) \cdot (\Delta H_{I,T}^{0} - 1.5 \cdot \mathrm{D.H.} + \mathrm{C}' \cdot I + \Delta c_{\mathrm{p}} \cdot \Delta T) \qquad (2)$$

$$\mathrm{D.H.} = z^* \cdot I^{0.5} / (1+1.5 \cdot I^{0.5}) \qquad (2a)$$

$$\mathrm{F}_1(T) = 52.23 \cdot (1/\theta - 1/T) \qquad (2b)$$

$$z^* = \Sigma\, (\mathrm{charges})^2_{\mathrm{reactants}} - \Sigma\, (\mathrm{charges})^2_{\mathrm{products}} \qquad (2c)$$

$$p^* = \Sigma\, (\mathrm{stoic.\ Coeff.})_{\mathrm{products}} - \Sigma\, (\mathrm{stoic.\ Coeff.})_{\mathrm{reactants}} \qquad (2d)$$

where log $K_{I,T}$ is the value of the equilibrium constants at any value of ionic strength (I) and temperature (T), log $K_{I,T}^{0,\theta}$ is the same value at infinite dilution ($I = 0$ mol dm^{-3}) and at the reference temperature ($T = \theta = 298.15$ K); C is an adjustable parameters for the ionic strength dependence of equilibrium constants; $\Delta H_{\mathrm{I,T}}^{0}$ is the enthalpy change of the given species at infinite dilution and at the reference temperature, C' and Δc_{p} are adjustable parameters for the ionic strength and temperature dependence of enthalpy changes. The two approaches are alternatives, but they carry the same chemical information. However, while the "conditional dataset" can only be used in the specific ionic medium considered, the "pure water dataset" allows the modelling of Zn^{2+} in any ionic medium containing the ions considered by the weak interactions, in every possible combination (*i.e.*, even in mixed media like many real aqueous systems).

[1] C.F. Baes, R.E. Mesmer, The hydrolysis of Cations. Wiley: New York, 1976.
[2] P.P.L. Brown, C. Ekberg, Hydrolysis of Metal Ions. Wiley-VCH: Weinheim (Germany), 2016.
[3] P.M. May, K. Muray, *Talanta* **1991**, 38, 1419.
[4] F. Crea, C. De Stefano, D. Milea, A. Pettignano, S. Sammartano, *Bioinorg. Chem. Appl.* **2015**, 2015, 267985.

Metal-coordinated assemblies of quercetin with a stimuli-responsive polymer: a solution equilibria study

Giuseppina D. G. Santonoceta, Carmelo Sgarlata

Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale A. Doria 6, 95125, Catania, Italy

Chemotherapy is still the most widely adopted therapeutic mode in cancer treatment; however, it is often invasive and shows intrinsic limitations such as low solubility, poor permeability and short biological half-life of some drugs which significantly reduce their application [1,2]. The development of drug delivery systems (DDSs) has emerged as a strategy to overcome the above drawbacks and to enhance the therapeutic efficacy by releasing chemotherapy agents at the tumor site and retarding the drug leaking into a healthy physiological environment [3].

Despite the remarkable improvement in the development of more efficient DDSs, a quantitative characterization of the molecular interactions between drugs and carriers in solution has been rarely addressed.

In this work, the study of multiple equilibria in solution is proposed as the key for the design and development of DDSs obtained by the co-assembly of polyacrylic acid (PAA), a biocompatible and pH-responsive polymer, metal ions of biological interest (Cu^{2+} and Zn^{2+}) and quercetin (Que), with the aim of optimizing the stability and the drug loading capability of the resulting assembly. It is well known that the pharmacological application of quercetin, a flavonoid with neuro/cardioprotective, anti-inflammatory and anticancer effects, is severely confined due to its low water solubility and *in vivo* bioavailability [4].

The flavonoid capacity to complex metal ions and polymer as well as the interaction of the quercetin metal complexes with PAA have been investigated by both UV-Vis spectroscopy and isothermal titration calorimetry (ITC) in neutral aqueous solution at 25 °C. Speciation models showed that Que can form 1:1 species with both metal ions and an additional 2:1 species with Cu^{2+} [5]. ITC measurements allowed for the determination of the thermodynamic parameters ($\Delta H°$ and $T\Delta S°$) that guide the formation of the complex species formed by Que with Cu^{2+} and Zn^{2+} in aqueous solution [6,7]. Interestingly, it was observed that although Que and PAA are unable to interact, the presence of the metal ion allowed for their interaction and thus its features resulted to be crucial for the formation of the final assembly. ITC and UV-Vis measurements mutually confirmed the species and stability of the Que-M-PAA systems in solution.

This study highlights the crucial role played by metal ions for the improvement of quercetin stability in aqueous solution and their ability to act as a bridge to associate a drug with a stimuli-responsive polymer. Data obtained provided a detailed understanding of the assembly formation mechanisms and the conditions which are essential to exert control over the design and performances of the resulting DDSs.

[1] H. Zhang, Y. Wu, X. Xu, C. Chen, X. Xue, B. Xu, T. Li, Z. Chen, *Polymers* **2021**, *13*(1), 67.
[2] J. Zhou, L. Rao, G. Yu, T.R. Cook, X. Chen, F. Huang, *Chem. Soc. Rev.* **2021**, *50*(4), 2839-2891.
[3] Q. Sun, M. Radosz, Y. Shen, *J. Control. Release* **2012**, *164*(2), 156-169.
[4] A. Samadi, M. Pourmadadi, F. Yazdian, H. Rashedi, M. Navaei-Nigjeh, *Int. J. Biol. Macromol.* **2021**, *182*, 11-25.
[5] S. A. Cherrak, N. Mokhtari-Soulimane, F. Berroukeche, B. Bensenane, A. Cherbonnel, H. Merzouk, M. Elhabiri, *PloS one* **2016**, *11*(10), e0165575.
[6] C. Sgarlata, V. Zito, G. Arena, *Anal. Bioanal. Chem.* **2013**, *405*, 1085-1094.
[7] G. Arena, P. Gans, C. Sgarlata, *Anal. Bioanal. Chem.* **2016**, *408*, 6413-6422.

Medium Optimization for Algal Culture in Bivalve Hatchery

Andrea Baldi [a], *Andrea Cailotto* [b], *Luisa Pasti* [a], *Leonardo Aguiari* [b]

[a] *Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, 44121-Ferrara, Italy.*
[b] *Naturedulis s.r.l., Piazzale Leo Scarpa 45, 44020 Goro (FE), Italy.*

Microalgae are of great importance since they play a central role in global geochemical cycles of carbon, nitrogen, phosphorus, sulfur, and silicon. They also represent a source of various compounds, that can be used in pharmaceutics, cosmetics, chemical, and energetic industries. In addition, they are employed in aquaculture feed applications processes, mainly in hatcheries. Indeed, bivalve hatcheries entirely depend on live microalgae as a food source for larval stages. Microalgae production is labour intensive, and the cost of microalgae production is generally 30–50 % of the total operational cost for a bivalve hatchery[1]. The efficient production and use of microalgae are therefore of great interest in bivalve production. Nutritional quality is the primary criterion for the choice of microalgae species for bivalve larvae culture, which, in turn is a function of optimal microalgae growth conditions.

The conditions required for microalgae growth, such as temperature, light intensity, pH values, concentration and composition of the culture medium influence their intracellular enzymes and organisms' function and finally their nutritional value. Among the different parameters that can influence the growth and biochemical composition of microalgal species, the culture medium plays a central role, especially for what concerns nitrogen content. The chemical composition of microalgal cells is also known to vary during their growth phase, particularly with respect to their lipid component. In this study, the effects of different culture media on microalgae growth and composition are investigated. In particular, culture media containing different amount of boron and microelements were considered. All experiments were conducted in photobioreactors in controlled conditions and Isochrysis Galbana (Parke; Clone T-ISO) microalgae species was selected to test the optimal culture medium. Wet algae samples were sampled at different times during the algal growth phases (induction, exponential, and stationary) the growth rate and the lipid content was determined. The preliminary results indicate that biochemical composition of microalgae is influenced by microelements concentrations in the culture media.

[1] P.C. Oostlander, J. van Houcke, R.H. Wijffels, M.J. Barbosa, Microalgae production cost in aquaculture hatcheries, Aquaculture Volume 525, 30 August **2020**, 735310

[2] Yue Gao, Chunyang Zhou, Camille Gaulier, Arne Bratkic, Josep Galceran, Jaume Puy, Hao Zhang, Martine Leermakers, Willy Baeyens. Labile trace metal concentration measurements in marine environments: From coastal to open ocean areas. *TrAC Trends in Analytical Chemistry*. **2019**. 92-101.

[3] Enver Güler, Cüneyt Kaya, Nalan Kabay, Müşerref Arda, Boron removal from seawater: State-of-the-art review, Desalination,Volume 356, **2015**, pages 85-93.

[4] Svetlana V. Smirnova, Dmitry V. Ilin, Igor V. Pletnev, Extraction and ICP-OES determination of heavy metals using tetrabutylammonium bromide aqueous biphasic system and oleophilic collector, *Talanta*. **2021**, Volume 221.

[5] Jens Søndergaard, Gert Asmund, Martin M. Larsen, Trace elements determination in seawater by ICP-MS with on-line pre-concentration on a Chelex-100 column using a 'standard' instrument setup. *Department of Bioscience, Aarhus University.* MethodsX**. 2015.** Volume 2, *Pages 323-330.*

[6] G. L. Foster, P. A. E. Pogge von Strandmann and J. W. B. Rae, Boron and magnesium isotopic composition of seawater, *Geochemistry. Geophysics. Geosystems***. 2010**, Volume 11, Number 8.

DNA-templated reactions controlled by biomolecules

Lorena Baranda Pellejero [a], *Francesco Ricci* [a]

[a] *Department of Chemistry, University of Rome, Tor Vergata, Rome, Italy*

In the crowded cellular environment, where thousands of different species coexist in a limited volume, it is of crucial importance to control chemical reactivity in a highly precise manner in order to avoid non-specific reactions that might lead to undesired effects. Faced with this challenge, Nature has evolved mechanisms that allow the co-localization of biomolecules in a confined volume, which results in an increase of their effective local concentrations. Such local concentration enhancement triggers intermolecular reactions that would otherwise be unlikely to occur at the low concentration levels found in cells [1].

Inspired by this mechanism, spatial co-localization of interacting species has been recreated in synthetic systems to control their reactivity. Taking advantage of the predictability of nucleic acids interactions, the possibility to direct chemical reactions using synthetic DNA strands as templates has been recently demonstrated, emerging as the field of DNA-templated synthesis (DTS) [2].
In this approach the reactive groups are conjugated to synthetic oligonucleotide sequences (DNA or RNA). The sequence-specific hybridization of these modified-sequences leads to co-localization of the reactive groups thus enabling chemical reactions under highly dilute conditions. Numerous applications of DTS have been reported, ranging from nucleic acid detection to drug-release [3, 4]. However, a critical limitation of DTS is that DNA-templated reactions rely solely on nucleic acids as templating agents. Triggering DNA-templated reactions with other biomolecules, including relevant clinical biomarkers, would increase both the versatility and utility of DTS and broaden the contexts in which chemical reactivity can be controlled.

Motivated by the above arguments, here we demonstrate a strategy for the control of DNA-templated chemical reactions using biomolecules such as protein biomarkers. To achieve this, we have designed synthetic DNA oligonucleotides conjugated to one end to reactive groups and to the other end to recognition elements specific for the biomolecule of interest. Only in the presence of this biomolecule, such DNA modified strands will be brought into close proximity favouring oligonucleotide hybridization and therefore triggering the reaction between the reactive groups that leads to the formation of the reaction product. The approach we propose here allows to control product formation in the presence of a specific biomolecule in concentration-dependent and in an orthogonal fashion. Since molecules of different nature (such as imaging agents, pharmaceuticals, etc) can be synthetized in the presence of a specific biomolecular marker, this strategy can in principle be used for different applications including in-situ drug production, imaging and diagnosis.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Actions grant agreement No 765703.

[1] Hobert, E. M., Doerner, A. E., Walker, A. S. & Schepartz, A. Effective molarity redux: proximity as a guiding force in chemistry and biology. *Isr. J. Chem.* **2013**, *53*, 567–576.
[2] Li, X. & Liu, D. R. DNA-templated organic synthesis: nature’s strategy for controlling chemical reactivity applied to synthetic molecules. *Angew. Chem. Int. Ed.* **2004**, *43*, 4848–4870.
[3] Di Pisa, M. & Seitz, O. Nucleic acid templated reactions for chemical biology. *ChemMedChem.* **2017**, *12*, 872–882.
[4] Kim, K. T., Angerani, S., Chang, D. & Winssinger, N. Coupling of DNA circuit and templated reactions for quadratic amplification and release of functional molecules. *J. Am. Chem. Soc.* **2019**, *141*, 16288–16295.

Effect of polymerization time on the binding proprieties of imprinted nanoparticles (nanoMIPs) obtained by solid phase synthesis

Matteo Chiarello[a], *Simone Cavalera*[a], *Fabio Di Nardo*[a], *Laura Anfossi*[a], *Claudio Baggiani*[a]

[a] *Dipartimento di Chimica, Università degli studi di Torino, Torino, Italy*

Imprinted nanoparticles (nanoMIPs) present several advantages respect to bulk imprinted materials, but, when prepared by traditional methods, their usefulness is limited as the approaches are costly or require complex optimization steps, while the purification from template molecules is challenging. An innovative approach is represented by the solid-phase synthesis [1]. The polymerization process, takes place in the interstitial space between non-porous glass beads grafted with template molecules. Once the polymerization process ends, unreacted monomers, polymerization by-products and low affinity polymers can be washed away, while the high affinity nanoMIPs bind strongly enough to be retained by the solid phase. NanoMIP are subsequently eluted by washing the solid phase with a solution capable of breaking the non-covalent molecular interactions.

This approach presents several practical advantages over traditional solution synthesis techniques: the bleeding effect due to residual template molecules in the imprinted polymer is avoided as the template is covalently grafted onto the solid phase. Grafted templates do not need to be soluble in the polymerization solvent, thus eliminating any issue about solvent-template compatibility. Solid phase can be reused many times, allowing the use of expensive molecule, Toxic or harmful templates confinement on the surface of the beads eliminates any health risks from residual template during the recover step of the imprinted nanoMIPs. The preparation of nanoMIPs by solid-phase synthesis has proven to be equally suitable for small molecules, peptides and proteins, living cells and viruses. Furthermore, it is very versatile, as the the experimental conditions necessary for a successful imprinting process can be changed according to current needs in a more flexible way than the solution synthesis technique [2].

While the traditional ways to synthetize MIPs are mature and robust, most of the parameters of solid phase synthesis are not yet sufficiently investigated. Here we present an explorative study about the effect of different polymerization times – ranging from 15 min to 3 hours – on the binding properties of ciprofloxacin-imprinted nanoMIPs. The binding properties were studied by partition equilibrium and rebind kinetic experiments to measure the binding affinity (K_{eq}) and the kinetic rate constants (k_d, k_a). Furthermore, selectivity and non-specific binding were evalued by measuring the rebinding of levofloxacin onto ciprofloxacin-imprinted nanoMIPs, and ciprofloxacin onto diclofenac-imprinted nanoMIPs, respectively. The results show that long polymerization times produces nanoMIPs with low affinity ($<10^5$ M^{-1}) and selectivity, while very short polymerization times strongly increase affinity ($>10^7$ M^{-1}) but not selectivity. Intermediate times (45-60 min) seems to be suitable to obtain nanoMIPs with high affinity ($>10^6$ M^{-1}) and good selectivity.

In conclusion, we demonstrate how optimizing polymerization times it is possible to obtain nanoMIPs with affinity and selectivity comparable to natural antibodies.

[1] F. Canfarotta, A. Poma, A. Guerreiro, S. Piletsky, *Nat. Protocols*, 11 (2016) 443–455.

[2] S. Cavalera, M. Chiarello, F. di Nardo, L. Anfossi, C. Baggiani, *React.Funct.Polym.* 163 (2021) 104893.

Smartphone-assisted electrochemical sensor modified for reliable detection of tyrosine in serum samples

Luca Fiore,[1] Vincenzo Mazzaracchio, [1] Benedetta De Lellis, [1] Fabiana Arduini [1,2] and Danila Moscone

1 Department of Chemical Science and Technology, University of Rome "Tor Vergata", Rome, Italy

2 Sense4Med S.r.l., Italy

L-Tyrosine (L-Tyr) is an important non-essential amino acid which is synthesized by the human body through hydroxylation of phenylalanine[1]. Furthermore, it is the precursor of important neurotransmitters such as epinephrine, norepinephrine, and dopamine, which regulate the main physiological functions[2]. Any disorders in the various metabolic pathways of this amino acid can cause its accumulation as in tyrosinemia[3] and alkaptonuria[4] diseases. The traditional and most-commonly used techniques to detect amino acids encompasses spectrophotometry, gas chromatography, liquid chromatography, high performance liquid chromatography, as well. However, these techniques are expensive, time-consuming, required laboratory set-up, and trained personnel. Herein, we propose a novel user-friendly and low cost miniaturised screen-printed sensor for the detection of tyrosine in human serum samples, using square wave voltammetry as electrochemical technique. The screen-printed electrodes were printed on a polyester substrate in order to realize a platform that can be used for measurements directly in situ. Moreover, the working electrode was modified via drop casting with a carbon black dispersion, in order to increase the electrochemical performance of this device in terms of sensitivity and low applied potential. Tyrosine quantification has been achieved with a detection limit of 6 µM and a linearity range up to 0.5 mM.

[1] A. Chakrapani, P. Gissen, P. McKiernan. Disorders of tyrosine metabolism. In Inborn metabolic diseases. Springer Sci. Rev. 2012, 265-276.
[2] Q. Xu, S. F. Wang. Electrocatalytic oxidation and direct determination of L-tyrosine by square wave voltammetry at multi-wall carbon nanotubes modified glassy carbon electrodes. . Microchimica Acta. 2005, 151(1-2), 47-52.
[3] F.J. Van Spronsen.. . Hereditary tyrosinemia type I: a new clinical classification with difference in prognosis on dietary treatment. Hepatology 20. 1994, 1187-1191.
[4] C. Phornphutkul et al. Natural history of alkaptonuria. N. Engl. J. Med. 2002, 347, 2111-2121.

A novel colorimetric assay for Levodopa detection in Parkinson's drugs

Mariagrazia Lettieri, Simona Scarano, Maria Minunni, Pasquale Palladino

Department of Chemistry "Ugo Schiff", University of Florence, 50019, Sesto Fiorentino, FI, Italy

Levodopa is the mainstay in the pharmacological therapy applied to treat patients who suffer of Parkinson's diseases [1]. The diagnosis of Parkinson's disease is confirmed by a concrete response to levodopa treatment. Parkinson's disorder is one of the most widespread diseases consisting in degeneration of dopaminergic neurons in the substantia nigra pars compacta. This results in a decrease of dopamine levels which leads to symptoms like muscle rigidity, hypo- and bradykinesia and resting tremor. A single oral dose of drug, containing levodopa, is able to improve drastically motor difficulties providing remarkable benefit in the patients. Levodopa is a pro-drug able to pass through the blood brain barrier and to be enzymatically converted in dopamine which acts directly on the degenerated dopaminergic neurons. Dopamine cannot be straightly administered since it is a polar molecule unable to cross the blood brain barrier. In addition, the administration of dopamine, at the peripheral level, causes various side effects such as hypotension and nausea. In order to avoid these problems, levodopa is the main active principle used in the fabrication of Parkinson's drugs. Furthemore, in the levodopa based drugs are introduced enzymatic inhibitor, like carbidopa or benserazide, to prevent levodopa conversion in dopamine before to reach the blood brain barrier. Here, a colorimetric assay able to quantify levodopa in Parkinson's drugs, was developed. The proposed detection strategy is based on the colorimetric product obtained by the reaction between levodopa, dissolved in dymethil sulfoxide, and magnesium acetate solubilized in ammonia solution. This reaction leads to the conversion of levodopa in a violet compound which enabled us to detect levodopa in drugs. Despite the drug matrix complexity, levodopa was selectively detected with highly reproducible performance. In addition, the presence of other important compounds, like carbidopa or benserazide, did not interfere with our analysis. The assay is applied to commercially available drug, from different suppliers. Currently, the most employed analytical tool for levodopa determination in drugs, is HPLC-MS[2]. For these reasons, the designed colorimetric assay could simplify Parkinson's drugs quality control, selectively quantifying levodopa.

[1] A. H. V. Schapira, M. Emre, P. Jenner, W. Poewe, *Eur. J. Neurol.* **2009**, *16*, 982–989.

[2] C. L. MU, D. WU, H. F. LU, H. XIE, Q. L. ZHANG, *Chinese J. Anal. Chem.* **2017**, *45*, e1726–e1733.

Establishing a protocol for routine airborne SARS-CoV-2 RNA indoor sampling and relation with possible infectivity

Sabina Licen[a,b], Lorenzo Martello[a,b], Anna Lilian Gardossi[d], Sabrina Semeraro[b], Jolanda Palmisani[c], Alessia di Gilio[c], Valentina Torboli[d], Alberto Pallavicini[d], Pierluigi Barbieri[a,b]

[a] *Dept. of Chemical & Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127, Trieste, Italy*
[b] *INSTM National Interuniversity Consortium of Materials Science and Technology, Via G. Giusti, 9 50121, Firenze, Italy*
[c] *Dept. of Biology, University of Bari "Aldo Moro", Via Via E. Orabona, 4 70124, Bari, Italy*
[d] *Dept. of Life Sciences, University of Trieste, Via L. Giorgieri 8, 34127, Trieste, Italy*

The relevance of airborne exposure to SARS-CoV-2 in indoor environments is a matter of research and debate, with special importance for healthcare low-risk settings. A recent review about indoor air sampling for virus detection [1] listed the variety of approaches found in literature: they differ in sampling device and collection support, sampling time, sampling flow, sampler positioning, particulate matter size range collection. Out of 25 studies, 10 found negative results in all collected samples, and 15 found at least one positive sample. The review authors concluded that, due to the very different sampling methods, it is difficult to compare the results of the studies. Thus there is a urge in establishing well defined protocols and equipment to face post-pandemic scenarios and to be prepared to possible future crises. On the other hand a routine control (24h/7d) can be possible and economically sustainable only if the sampling procedure require affordable equipment and samples analysis can be carried out by routine protocols already in use in public facilities.

Recently we published a study conducted collecting 24-h PM_{10} samples in a COVID-19 geriatric ward by a low noise (<35 dB) air sampler (SILENT Air Sampler—FAI Instruments S.r.l) on quartz fiber filters operating at a flow rate of 10 L/min. The detection of E and RdRp genes was performed by RT-qPCR. The possible infectivity was related to Vero E6 cells response to COVID-19 positive nasopharyngeal swab extracts: only the extracts with a viral load above E^{+10} viral copies (approximately Ct<24) have been able to establish a persistent infection in vitro. Therefore we considered that the cytopathic effect, could be considered unlikely for the environmental PM_{10} samples we collected which showed a Ct between 36 and 39 [2].

In this study we present a protocol for the assessment of recovery in real sampling conditions using the above mentioned device and filters spiked with a standard SARS-CoV-2 RNA solution (EURM-019, single stranded RNA fragments of SARS-CoV-2, European Commission Joint Research Centre). The experiments have been carried out during several days in a 5 x 5 x 3 m room, operating 4h hours to 24 hours sampling, recording room temperature and humidity at one minute intervals. Sampled filters have been stored at -80°C. Three replicates of blank samples and "field" samples have been also analyzed. Every RNA analysis has been carried out on half filters to evaluate extraction and analysis uncertainty.

[1] J. T., Borges, L. Y., Nakada, M. G., Maniero, & J. R., Guimarães *Environmental Science and Pollution Research* **2021**, 1-14.

[2] P. Barbieri, L. Zupin, S. Licen, V. Torboli, S. Semeraro, S. Cozzutto, J. Palmisani, A. Di Gilio, G. de Gennaro, F. Fontana, C. Omiciuolo, A. Pallavicini, M. Ruscio, S. Crovella, *Environmental Research* **2021**, 198,111200

FPSE-HPLC-PDA determination of UV filters in biological matrices

M. Locatelli[a], *A. Tartaglia*[a], *C. D'Ovidio*[b], *E. Rosato*[a], *M. Bonelli*[b], *K.G. Furton*[c], *A. Kabir*[c]

(a) Department of Pharmacy, University of Chieti–Pescara "G. d'Annunzio", Via dei Vestini 31, Chieti 66100, Italy; (b) Department of Medicine and Aging Sciences, Section of Legal Medicine, University of Chieti–Pescara "G. d'Annunzio", Chieti 66100, Italy; (c) Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th St, Miami, FL 33199, USA

Prolonged human exposure to solar UV radiation may result in acute and chronic health effects on the skin, eye and immune system (e.g. sunburns, skin cancers, cataracts, etc.). For this reason, there is a greater interest in minimizing solar UV radiation exposure and UV filters are incorporated in sunscreens formulations as well as in daily use cosmetics. UV filters, despite they are designed for external use, can be absorbed through the skin and different undesirable effects have been attributed to these compounds; thus, sensitive analytical methods to monitor biological levels of these compounds are in great demand.

The present poster describe an high performance liquid chromatography-photodiode array detection (HPLC-PDA) method for the simultaneous analysis of six benzophenone derivative UV filters including benzophenone (BZ); 5-Benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid (BP-4); 4,4′-Dihydroxybenzophenone (4-DHB); 2,2′,4,4′-Tetrahydroxybenzophenone (BP-2); 2,4-dihydroxybenzophenone (BP-1); and 2,2′-Dihydroxy-4-methoxybenzophenone (DHMB) [1]. Chromatographic separation was conducted using a Spherisorb ODS 1 (C18) column in isocratic elution mode with a run time less than 25 minutes. The method was validated, in accordance with international guidelines, in the range from 0.1 to 10 µg/mL for all the UV filter compounds. Propyl 4- hydroxybenzoate was used as the internal standard (IS). The limit of quantification (LOQ) was 0.1 µg/mL, while limit of detection (LOD) was 0.03 µg/mL. The weighted-matrix matched standard calibration curves of six UV filters showed a good linearity up to a concentration of 10 µg/mL.

Prior to the HPLC-PDA analysis, these compounds were extracted from biological fluids (human whole blood, plasma and urine) through an innovative extraction technique, fabric phase sorptive extraction (FPSE). This new sample preparation technique, introduced in 2014, allows extraction of analytes through a direct contact between FPSE device and sample. The devices are constituted of natural or synthetic permeable and flexible substrate, chemically coated with a sol-gel organic-inorganic hybrid sorbent. This approach exhibits high recovery for the target analytes and allowed to reduce the amount of used organic solvents.

Additionally, fabric phase sorptive extraction membrane has been evaluated as a viable alternative to "dried blood spot card (DBS Card)" to collect droplets of whole blood spiked with the target UV filters and stored for a prolonged period after drying. The dried blood spots collected onto the FPSE membranes were found stable during the evaluated period up to 40 days with the analyte retention data comparable to the data obtained from whole blood droplets onto the FPSE membrane without prolonged storage.

[1] M. Locatelli, K.G. Furton, A. Tartaglia, E. Sperandio, H.I. Ulusoy, A. Kabir, An FPSE-HPLC-PDA method for rapid determination of solar UV filters in human whole blood, plasma and urine, J. Chromatogr B 1118-1119 (2019) 40-50.

Ultra-small octahedral PtNP-labeled antibodies as an ultrasensitive nanozyme probe for chemiluminescence detection in bioanalytics

Mauro Moglianetti[a], Luisa Stella Dolci[b], Barbara Roda[b,c], Valentina Marassi[c], Anna Scarsi[d,e], Deborah Pedone[d], Pier Paolo Pompa[d], Andrea Zattoni[b], Pierluigi Reschiglian[b], Aldo Roda[b]

[a] HiQ-Nano s.r.l., Via Barsanti 73010 Arnesano (LE;) [b] INBB – Biostructures and Biosystems National Institute-Rome, Italy; [c] Department of Chemistry G. Ciamician, Alma Mater Studiorum-University of Bologna, Italy; [d] Nanobiointeractions & Nanodiagnostics, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy; [e] Department of Chemistry and Industrial Chemistry, University of Genova, 16146 Genova, Italy

Chemiluminescence (CL)-based probes are one of the most sensitive detection principles in nanodiagnostics. A widely used system is the CL substrate for peroxidase (HRP) employed to label a variety of molecules ranging from small steroids to protein. The CL cocktail for HRP is based on luminol or its analogues, hydrogen peroxide, and an enhancer, allowing the detection of submolar concentrations of the enzyme-labeled analyte. The catalyst of the CL reaction, namely HRP, can be replaced by other more practical and highly stable nano-catalysts/nanozymes; among them, recent studies have demonstrated the superior performance of Pt nanomaterials [1]. In this work, we propose the use of ultra-small (3 nm) citrate-coated octahedral Pt nanocrystals prepared by a new wet chemical reduction method in aqueous environment and conjugated to a secondary human IgG antibody, as an ultrasensitive probe for luminol/hydrogen peroxide CL detection. Conjugates with different nanocrystal-to-antibody molar ratios were first fully characterized and purified by Field-Flow Fractionation (FFF) [2]. FFF confirms the homogeneous size of the conjugated which represents a fundamental parameter for their efficiency. The FFF-selected purified conjugates are homogeneous in size and highly concentrated, and readily available for downstream CL tests, an important requirement for the use of FFF as semi-prep step. First results demonstrate the applicability of Pt nanocrystals as probes for CL detection. Indeed the Pt nanocrystals-antibodies CL signal has been measured for the different nanoparticles-IgG molar ratios, showing an increasing signal as a function of nanoparticles concentration with the possibility to detect IgG down to 10^{-12} M, value close to that obtained using HRP [3]. In addition, the light signal reaches a steady state value for more than 30 minutes, thus facilitating the assay handling. These results pave the way to the use of Pt nanomaterials, highly monodisperse in size and shape and with easy-to-remove coating, for the production of highly efficient catalysts/nanozymes for CL applications and the development of simple and rapid new tests.

[1] M. Moglianetti, E. De Luca, D. Pedone, R. Marotta, T. Catelani, B. Sartori, H. Amenitsch, S. F. Retta and P. P. Pompa, *Nanoscale*, **2016**, *8*, 3739-3752
[2] V. Marassi, D. Calabria, I. Trozzi, A. Zattoni, P. Reschiglian and B. Roda, *Journal of Chromatography A*, **2021**, *1636*, 461739
[3] A. Roda, F. Arduini, M. Mirasoli, M. Zangheri, L. Fabiani, N. Colozza, E. Marchegiani, P. Simoni and D. Moscone, *Biosensors and Bioelectronics*, **2020**, *155*, 112093

Multiplexing Chemiluminescent Single Molecule Analysis based on Digitalized Enzyme-Linked Immunosorbent Assay (ELISA)

Cecilia Scandurra[a,c], *Eleonora Macchia*[b], *Paolo Bollella*[a], *Luisa Torsi*[a,b,c]

[a] *Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", 70125 Bari (Italy),*
[b] *The Faculty of Science and Engineering, Åbo Akademi University, 20500 Turku (Finland),*
[c] *CSGI (Centre for Colloid and Surface Science), 70125 Bari (Italy)*

cecilia.scandurra@uniba.it

Disease detection at the molecular level plays a key role in the early diagnosis and treatment. A challenge facing the field is that protein biomarkers for early diagnosis can be present in very low abundance. The lower limit of detection with conventional immunoassay technology is in the upper femtomolar range (10^{-13} M). In this regard, digital immunoassay technology has improved detection sensitivity of about three logs, to the attomolar range (10^{-18} M). This can potentially open new avenues in diagnostics and therapeutics [1].

Herein, we have developed a protocol for the detection and quantification of IgG, IgM and C-reactive protein (CRP) in multiplexing fashion, developing a customized planar array that could help with a correct statistical analysis to define the level of inflammation and the urge for medical assistance [2,3]. Unlike the traditional ELISA sandwich, we have assay plates spotted with an immobilized anchor antibody (capturing antibody) in each of 96 microwells. At first, we immobilized the biorecognition antibody by means of an affinity interaction towards a peptide-tag that was covalently linked to the biorecognition antibody. Next, the antigen is sandwiched between the peptide-tagged capture and a biotinylated detector antibody. The formation of the immunocomplex is detected through the reduction of H_2O_2 catalysed by Streptavidin Horseradish Peroxidase (SA-HRP) bound to the biotylinated antibody, in presence of luminol that is converted to 3-aminophthalate dianion, resulting in a chemiluminescent output [4].

Finally, we performed IgG, IgM and CRP quantification also in body fluids (e.g., serum, saliva etc.) to demonstrate the possibility to perform multiplexing analysis in such complex systems.

References

[1] D. H. Wilson, D. M. Rissin, C. W. Kan, D. R. Fournier, T. Piech, T. G. Campbell, R. E. Meyer, M. W. Fishburn, C. Cabrera, P. P. Patel, E. Frew, Y. Chen, L. Chang, E. P. Ferrell, V. von Einem, W. McGuigan, M. Reinhardt, H. Sayer, C. Vielsack, D. C. Duffy, *J. Lab. Autom.*, **2016**, 21(4), 533-547.

[2] C. P. Souza, J. R. Schissler, E. T. Contreras, S. W. Dow, L. S. Hopkins, J.W. Coy, R. A. W. Rosychuk, J.R. Hawley, M. R. **2018**, *Adv. Vet. Dermatol.*, 29(6), 482-e162.

[3] S. M. Churchman, J. Geiler, R. Parmar, E. A. Horner, L. D. Church, P. Emery, M. H. Buch, M. F. McDermott, F. Ponchel. **2012**, *Clin. Exp. Rheumatol.*, 30(4), 534-42.

[4] C. I. Tobos, S. Kim, D. M. Rissin, J. M. Johnson, S. Douglas, S. Yan, S. Nie, B. Rice, K. Sung, H. D. Sikes, D. C. Duffy, **2019**, *J. Immunol. Methods*, 474, 112643.

Rapid salivary and serum IgA detection with dual lateral flow optical/chemiluminescence immunosensors in patients with COVID-19 disease add diagnostic value: a debate for perplexed scientists

Aldo Roda[a,f], Simone Cavalera[e], Fabio Di Nardo[e], Alessia Silla[c], Angela Punzo[a], Sergio Rosati[d], Patrizia Simoni[b], Barbara Colitte[e], Claudio Baggiani[e], Matilde Roda[d], Laura Anfossi[e]

[a]*Dept. of Chemistry Giacomo Ciamician,* [b]b *Dept. of Medical and Surgical Sciences,*
[c]*Dept. of Biomedical and Neuromotor Sciences* [d]*Dept, of Experimental, Diagnostic and Specialty Medicine University of Bologna,*
[e]*Dept. of Chemistry,* [c]*Dept of Veterinary Science, University of Turin,*
[f]*INBB, Biostructures and Biosystems National Institute, Rome, Italy*

Among the scientific community there is an active debate whether millions of cheap, fast diagnostic kits will help control the COVID-19 pandemic. These rapid paper-based tests using on nasal or throat swabs are thought of as tests of infectiousness, not of infection since they can detect high viral loads, missing many people with lower levels of the SARS-CoV-2 virus. Moreover, they are useful to curb the pandemic by quickly identifying the most contagious people, who might pass on the virus.

It is partially known that during a SARS-CoV-2 infection, the amount of virus rises and falls. PCR-based tests can pick up small amounts of viral genetic material, so can be positive even after a person stops being infectious. Rapid antigen tests detect the presence of viral proteins if the target antigen is present in sufficiently high concentrations so when a person is infected. Moreover, the limited period of time has limited the deep understand of the virus activity. To improve the accuracy of the COVID-19 infection diagnose and its time-dependent progression, the determination of immunoglobulin (Ig) A specific to SARS-CoV-2 (IgA secreted) in saliva and serum is important to complement the commonly used tests that detect IgG and IgM. We have developed a dual optical/chemiluminescence lateral flow immunoassay (LFIA) immunosensor for IgA in serum and saliva using a recombinant nucleocapsid antigen specifically captures SARS-CoV-2 antibodies in patient specimens and a labeled anti-human IgA reveals the bound IgA fraction. A dual colorimetric and chemiluminescence detection enables the affordable and ultrasensitive determination of IgA using a simple smartphone-photocamera to measures the colour signal provided by nanogold-labelled anti-human IgA. For the ultrasensitive chemiluminescence transduction, we used a contact imaging portable device based on cooled CCD, and measured the light signal resulting from the reaction of the HRP-labelled anti-human IgA with a H_2O_2/luminol/enhancers substrate. A total of 25 serum and 25 saliva samples from infected and/or recovered individuals were studied by the colorimetric LFIA, which was sensitive and reproducible enough for the semi-quantification of IgA in subjects with a strong serological response and in the early stage of COVID-19 infection. Switching to CL detection, the same immunosensor exhibited higher detection capability, revealing the presence of salivary IgA in infected individuals. Salivary IgA correlated with the time elapsed from diagnosis and the severity of the disease and could be increase the accuracy for early monitoring immune responses and for more accurate investigation of the prognostic utility in large-scale screening to assess the efficacy of SARS-CoV-2 vaccines.

[1] A. Roda, S. Cavalera, F. Di Nardo, D. Calabria, S. Rosati, P. Simoni,…& L.Anfossi
Biosensors and Bioelectronics 172 (2021) 112765

Multiclass determination of β-lactam drugs in urine by solid-phase extraction on Strata-X followed by HILIC-UV

Andrea Speltini[a,b], Jacopo Montagna[b], Francesca Merlo[a], Federica Maraschi[a], Antonella Profumo[a]

[a] *Department of Chemistry, University of Pavia, via Taramelli 12, 27100 Pavia;*
[b] *Department of Drug Sciences, University of Pavia, via Taramelli 12, 27100 Pavia.*

β-lactams represent one of the most important class of antimicrobial drugs, widely used in human medicine against Gram-positive and Gram-negative bacteria to treat respiratory tract infections. Being these compounds excreted mostly in their unchanged form in urine, this is a valuable and effective biological matrix for therapeutic drug monitoring [1,2].

Aim of this work is the development of a method joining multiclass determination of these antibiotics in human urine by solid-phase extraction (SPE) prior to quantification by high-performance liquid chromatography with UV detection (HPLC-UV). β-lactam drugs were selected among the most prescribed ones, including cephalosporins, penicillins, carbapenems and β-lactamase enzyme inhibitors that are usually formulated in combination with penicillins.

For the chromatographic separation, a hydrophilic interaction liquid chromatography (HILIC) column (4.6 × 250 mm, 5 μm, silica-linked zwitterionic sulfobetaine groups) proved to be valuable for the analysis of the four classes of these highly hydrophilic compounds. Proper selection of the chromatographic conditions, i.e. flow rate, pH, use of buffers, aqueous organic acid amount and gradient elution, afforded suitable capacity factors, peak shape and resolution.

Sample treatment was performed on commercial Strata-X SPE cartridge (200 mg, 3 mL), a functionalized divinylbenzene polymer embedding piperidone moieties, not yet tested for extraction/cleanup of these drugs in biological samples. SPE tests were first undertaken on 1-2 mL water samples to explore the adsorption/desorption conditions, then experiments were moved on real human urine (native pH and pH 2.5) before and after fortification (μg/mL levels). After extraction, washing with acidic aqueous methanol removed matrix co-extracted interferences, and analytes were eluted by methanol with and without addition of formic acid (2% v/v). Preliminary data indicate good recovery for most analytes and satisfying cleanup, advantageous for the subsequent HPLC-UV detection (230 and 290 nm).

Experiments are now underway to refine the SPE procedure for improving recovery and cleanup, before application to urine blind samples.

[1] E.A.A. Hamed, R.A.S. Salam, G.M. Hadad, *RSC Adv.* **2016**, *6*, 9465.
[2] P. Van Toi, K.V. Doan, N.N.Q. Minh, P.N. Phuoung, M.D. de Jong, H.R. van Doorn, T. Pouplin, *Biomed. Chromatogr.* **2020**, *34*, e4699.

Multiresidue Analysis of Aromas in White Wine by Means of Gas Chromatography Coupled with Mass Spectrometry

Ettore Guerriero[a], Massimo Iorizzo[b], Marina Cerasa[a], Ivan Notardonato[b], Bruno Testa[b], Francesco Letizia[b], Alessia Iannone[b], Cristina Di Fiore[b], Mario Vincenzo Russo[b], Pasquale Avino[b]

[a] *Institute of Atmospheric Pollution Research (IIA), National Research Council (CNR), Rome Research Area-Montelibretti, I-00015 Monterotondo Scalo, Italy.*

[b]*Department of Agricultural, Environmental and Food Sciences (DiAAA), University of Molise, Via De Sanctis, I-86100 Campobasso, Italy.*

Corresponding Author: *ivan.notardonato@scuolecasacalenda.edu.it*

Aromas are one of the most important parameters, which are able to influence the sensorial quality of white wines. The aromatic characteristics of white wines are in partly due to volatile compounds, releasing during the winemaking process [1]. The paper would like to show a direct injection into GC-MS/QqQ for the determination of secondary aromas in white wine samples fermented in two different ways. The procedure has been compared with more traditional methods used in this field, i.e., headspace analysis, liquid–liquid extraction and SPE extraction [2]. The application of such direct injection, for the first time in the literature, allows us to analyze Volatile Organic Compounds (VOCs) in the range 0.1–100 µg mL^{-1}, with Limits of Detection (LODs) and Limits of Quantification (LOQs) between 0.01–0.05 µg mL^{-1} and 0.03–0.09 µg mL^{-1}, respectively, intraday and interday below 5.6% and 8.5%, respectively, and recoveries above 92% at two different fortification levels. The procedure has been applied to real white wine samples: it evidences how the fermentation in wood cherry barrel yields higher VOC levels than ones in wine fermented in steel tank, causing production of different secondary aromas and different relative flavors. This may be because the cherry wood is characterized by the presence of tannins, catechin, phenolic acids and flavonoids and their esterification products useful to identify the origin of wine [3].

[1] Naranjo A., Martìnez-Lapuente L., Ayestarán B., Guadalupe Z., Pérez I., Canals C., Adell E., Beverages. **2021**, 7, 10.

[2] Russo M.V., Notardonato I., Cinelli G., Avino P., Anal. Bioanal. Chem. **2012**, 402(3), 1373-1381

[3] Costa M., Fontes L., Correia A. C., Miljić U., Jordão A. M., OENO One. **2020**, 54(4), 1159-1181

Determination of rare earth elements by ICP-MS: optimization of an analytical method for agrifood samples

R. Paparo [a*], *G. Di Natale* [c], *A. Di Nunzio* [a], *A. Giarra* [a], *G. Pagano* [a], *M.Toscanesi* [a], *G. Carotenuto* [b], *M. Trifuoggi* [a]

[a] *Department of Chemical Sciences, University of Naples Federico II, Via Cintia – 80126, Naples, Italy.*

[b] *IPCB-CNR, Piazzale E.Fermi, 1 - 80056, Portici (NA). Italy.*

[c] *Centro Servizi Metrologici e Tecnologici Avanzati (CeSMA), Complesso Universitario di Monte Sant'Angelo, Via Cintia - 80126 Naples, Italy*

**correspondence: ros.paparo@studenti.unina.it; 334-9730138*

Rare Earth Elements (REEs) have undergone a steady spread in several industrial, agricultural and zootechnical applications. Consequently, the attention concerning the REE-related health effects increased simultaneously with their industrial growth. Nevertheless, research findings display an apparent controversy regarding REE-associated health effects [1].

The data seem to highlight either favourable or adverse effects after REEs exposure. Several studies have demonstrated that REEs, like other xenobiotics, follow hormetic concentration-related trends, implying stimulatory or protective effects at low levels, then adverse effects at higher concentrations [2]. For this reason, it is important to investigate REE concentrations in different matrices to evaluate human exposure and environmental risk of these emerging contaminant.

Studies in literature show that in agriculture, REEs mixture has been used (as fertilizers), for more than 30 years, to improve the nutrition of plants [3]. Furthermore, supplementation of rare earth elements positively affects both animal growth and feed conversion efficiency (FCE) of pigs and poultry kept [4].

The aim of this study is to evaluate the presence and the levels of 16 REEs (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) in agricultural and zootechnical environment, more precisely: in fertilizers, pet-food, feed and animal organs. Hence, different digestion methods were performed, on Certified Reference Materials, to evaluate the best REEs extraction procedure. Then, about fifty both Italian and foreign agri-food samples, were digested with these procedures to assess REEs recovery. Additionally, accurate and specific ICP-MS methods were developed depending on the expected REEs concentrations.

In particular, to analyse solutions deriving from different digestion procedures two different sets of parameters were used: one specific for the determination of the elements present in solution at low concentration (High Sensitivity Mode, HS) and the other specific for those at high concentration (Normal Sensitivity Mode, NS). The Limit of Detection (LOD) in HS mode is in the range of (0,001...0,25 µg·L-1) and in NS mode is in the range of (0,025...3,11) µg·L-1.

The study confirmed the presence of REEs with a very variable range concentration, from 0,001 to 6509 mg/kg in the analysed agri-food samples. In conclusion, given the wide use of REEs in several fields and considering our findings, they should be monitored for a possible animal and human harmful effect.

References

[1] G. Pagano. Rare earth elements in human and environmental health. *Pan Stanford Publishing*. **2016**.

[2] G. Pagano, M. Guida, F. Tommasi, R. Oral. Health effects and toxicity mechanisms of rare earth elements—Knowledge gaps and research prospects. *Ecotoxicology and environmental safety.* **2015**, *115*, 40-48.

[3] Z. Hu, H. Richter, G. Sparovek, E. Schnug. Physiological and biochemical effects of rare earth elements on plants and their agricultural significance. *Journal of plant nutrition.* **2004**, *12*, 183-220.

[4] M. Q. Wang, Z. L. Xu. Effect of supplemental lanthanum on the growth performance of pigs. *Asian-Australasian Journal of Animal Sciences*. **2003**, *16*, 1360-1363.

Optimization of non-dioxin-like PCB analyses in milk samples by Box Behnken design

Valeria Nardelli[a], Valeria D'Amico[a], Ines Della Rovere[a], Francesco Casamassima[a], Wadir Mario Valentino Marchesiello[b], Donatella Nardiello[b], Maurizio Quinto[b,c]

[a] Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata, Via Manfredonia 20, Foggia 71121, Italy, [b] DAFNE - Department of Agriculture, Food, Natural resources, and Engineering - Università degli Studi di Foggia, Via Napoli, 25 - 71122 Foggia (Italy), [c] Department of Chemistry - Yanbian University, Park Road 977, 133002 Yanji, Jilin Province (China)

A multivariate optimization process of the sample extraction procedure by Box-Behnken design through a global desirability function [1] is described for the determination of six non-dioxin-like polychlorinated biphenyls (NDL-PCBs # 28, 52, 101, 153, 138 and 180) in milk by GC-ECD and mass spectrometry [2]. Three factors were involved in refining the extraction conditions: the acetone percentage in the extraction mixture, the sample/solvent ratio, and the extraction time. The three-factor design required 26 experiments that were carried out in duplicate and in a randomized order to minimize the bias effects of uncontrolled variables. The optimized factors (acetone percentage: 30%; sample-to-solvent ratio: 0.11 g mL^{-1}; extraction time: 45 min) ensured a low solvent consumption and a reduced extraction time, allowing a rapid and simultaneous preparation of multiple sample extracts. The method was validated according to the European directives (Decision 657/2002/EC, SANTE 2017/11813/EC) through the evaluation of linearity, selectivity, LOD, LOQ, recovery, precision, and ruggedness.

[1] S.L.C. Ferreira, R.E. Bruns, H.S. Ferreira, G.D. Matos, J.M. David, G.C. Brandão, E.G.P. da Silva, L.A. Portugal, P.S. dos Reis, A.S. Souza, W.N.L. dos Santos, *Anal. Chim. Acta* **2007**, *597*, 179.

[2] V. Nardelli, V. D'Amico, I. Della Rovere, F. Casamassima, W.M.V. Marchesiello, D. Nardiello, M. Quinto, *Emerging Contaminants* **2020**, *6*, 303.

Fraud in the fruit juice sector: a case study

Sabatino L., Scordino M., Scarangella M., Gambino G.L., Lazzaro F., Borzì M.A., Caruso R., Fiorillo M., Traulo P., Gagliano G.

Ministero delle Politiche Agricole Alimentari e Forestali (MiPAAF) - Dipartimento dell'Ispettorato centrale della tutela della qualità e della repressione frodi dei prodotti agroalimentari (ICQRF) - Laboratorio di Catania

This paper reports results of the "2019 - BAD JUICE" investigation carried out by the ICQRF inspectors and by the militaries of the “Guardia di Finanza” of Pisa. An amount of 1'411 tons of adulterated and falsely designated *organic apple juice* were seized with a total value of the confiscate commodities of 4'850'000 euros.

The ICQRF Catania Laboratory has verified a wide spectrum of chemical parameters of the samples under investigation, through different analytical techniques (HPLC-PDA/MS, GC-MS, IC, Amino Analyzer, IRMS, SNIF-NMR, etc.) by comparing the values obtained with the characteristics of apple juices reported in the reference guidelines of the European Fruit Juice Association [1].

The results obtained showed a low content of amino acids, organic acids, cations and anions characteristic of apple juices, as well as the absence of polyphenols. Furthermore, the values of the isotope ratios were outside the natural variability range defined for apple juices. Data results are compatible with a mixture of sugary substances obtained from plants with photosynthetic cycle C3, such as beet, and C4, such as cane and/or maize.

The investigative activity made possible to stop the criminals involved in the illicit production and marketing of concentrated apple juice. These juices, sophisticated with water and sugary substances and falsely declared organic of European origin, were used as ingredient to produce fruit juices, beverages, jams and conserves.

[1] Guideline for Apple Juice, European Fruit Juice Association 6.3. **2016**, 1-6.

Determination of differences in the volatile fingerprint of beers using a headspace solid-Phase microextraction gas chromatography quadrupole time-of-flight mass spectrometry system

Fabio Salafia[a,*], *Sonia Carabetta*[a], *Pietro Andronaco*[a] ,*Rosa Di Sanzo*[a], *Mariateresa Russo* [a]

[a]*Food Chemistry, Safety and Sensoromic Laboratory (FoCuSS Lab), Department of Agriculture, University "Mediterranea" of Reggio Calabria, Via dell'Università, 25, 89124 Reggio Calabria, Italy.*

**fabio.salafia@unirc.it*

Aroma of beers is determined by the raw materials used (malts, hops and yeasts). The aromatic variations that can be obtained are endless due to the numerous raw materials on the market, but it is possible to identify targhet molecules to be used to discriminate beer styles [1].

The aim of this work was to use the headspace solid-Phase microextraction (HS-SPME) technique coupled to a gas chromatography (GC) system with quadrupole time-of-flight mass spectrometry (QTOF/MS) to characterize the aromatic profiles of different beers, identifying volatile fingerprints to differentiate the main styles of beer and determine the degree of aging of the products.

HS-SPME sampling was done by an automated preparative system coupled to the GC-QTOF/MS using a Divinylbenzene/Carboxen/PDMS fiber with dimension 50/30 µm.

The beers were analyzed immediately after opening the product to best preserve the aromatic component. Five replicates, under optimal conditions, were made for all samples, obtaining an aromatic profile as authentic as possible.

Numerous alcohols, aldehydes, amines, esters, alkylated phenols, hydrocarbons and terpenes were identified in the analyzed beers. Some of these molecules have been used as target molecules to build the volatile fingerprint of beers.

The data obtained were processed with statistical analysis to confirm the relationship between analyzed samples and volatile compounds.

[1] J. Jiao, N. Ding, T. Shi, X. Chai,1 P. Cong, Z. Zhu, *Anal. Lett.* **2011,** *4*, 44.

Determination of coumarins, furocoumarins and polymethoxyflavones in cold-pressed *Citrus* essential oils using SFC-QqQ

M.R. Testa Camillo [a], *M. Russo* [a], *A. Arigò* [a], *P. Dugo* [a,b], *L. Mondello* [a,b,c,d]

[a] *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, 98168, Italy;*
[b] *Chromaleont s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, 98168, Italy;*
[c] *Department of Sciences and Technologies for Human and Environment, University Campus Bio-Medico of Rome, Rome, 00128, Italy;*
[d] *BeSep s.r.l., c/o Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina, 98168, Italy.*

Coumarins (C), furocoumarins (FC) and polymethoxyflavones (PMF) are a class of oxygen heterocyclic compounds present in cold-pressed *Citrus* essential oils.[1] These compounds are present in plants and in the peels of fruit of the *Citrus* genus. They possess numerous pharmacological and pharmacotherapeutic activities, including anticoagulant, anti-inflammatory, antiviral and antitumoral action. However, the ingestion of large quantities or the interaction with UVA radiations could be toxic to human health. For these reasons, investigation of these compounds has become of great interest for the food, pharmaceutical and cosmetical sectors.

Liquid chromatography coupled with photodiode array or mass spectrometer detectors represent the analytical technique normally employed for the analysis of oxygen heterocyclic compounds compounds. According to literature data [1], supercritical fluid chromatography (SFC) could represent a valid alternative for the determination of these molecules. To the best of our knowledge there is a lack of investigation of oxygen heterocyclic compounds through the use of SFC in *Citrus* essential oils.

The present research is focused on the development of a rapid analytical method with a low impact on the environment, through the use of SFC coupled to triple quadrupole mass spectrometry detector (QqQ).

For this purpose, seven chromatographic columns packed with different stationary phases were tested, such as C18, LC-NH_2, OH, ES-CN, Phenyl-Hexyl, Hilic and F5. Between stationary phases tested the F5 column, having a polar stationary phase, allows the best baseline separation of these molecules in eight minutes with the use of less than 10% of methanol.

Calibrations curves of thirty C, FC, PMF reference materials were constructed in order to quantify oxygen heterocyclic compounds in real sample. Method was validated calculating linearity, limit of detection, limit of quantification, accuracy, intraday and interday precision.

This fast method was successfully employed for the quantification of C, FC and PMF in cold-pressed *Citrus* essential oils.

[1] M. Russo, F. Rigano, A. Arigò, P. Dugo, L. Mondello, *J ESSENT OIL RES,* **2020***,* 51.

Synthesis and analytical characterization of silicon nanowires decorated with gold nanoparticles

Margherita Izzi[a], Rosaria Anna Picca[a], Antonio Alessio Leonardi[b,c], Maria Josè Lo Faro[b,c], Maria Chiara Sportelli[a], Alessia Irrera[c], Nicola Cioffi[a]

[a] Chemistry Department, University of Bari Aldo Moro, via E. Orabona 4, 70126 Bari, Italy; [b] Physics Department, University of Catania, Via Santa Sofia 64, Catania 95123, Italy; [c] IPCF-CNR, viale F. Stagno d'Alcontres 37, 98158 Messina, Italy.

Hybrid nanomaterials combining semiconductor and metal nanostructures represent an efficient way to develop novel platforms for advanced applications, ranging from sensing to catalysis [1–3]. In particular, silicon nanowires (SiNWs) decorated with metal nanoparticles (MeNPs) could be successfully exploited in analytical and sensing applications. SiNWs exhibit excellent characteristics such as large surface area, relatively high mechanical stability, and low cost [4]. Their modification with MeNPs ensures a strong improvement in the electric and optical signals, providing up-and-coming substrates for potential optical sensors or Surface-Enhanced Raman Spectroscopy. SiNWs are prepared by a wet-etching technique, assisted by the deposition of an ultrathin metal film on (p-, n-doped or highly doped) Si single crystal. SiNWs with very high density and controllable aspect ratios can be obtained. In the last years, we have studied the decoration of the proposed SiNWs with different MeNPs, including gold nanoparticles (AuNPs), by pulsed laser deposition [2,3]. This technique allows for loading “naked” NPs on the NWs. As alternative approaches, wet-methods can be used to decorate the semiconductor nanostructures. In this communication, we report on the modification of SiNW platforms by electrophoretic deposition (EPD) of chemically produced AuNPs. We exploit an innovative synthesis based on stainless steel as solid reductant for $HAuCl_4$ to prepare AuNPs [5,6]. This method is very easy, quick, cost-effective, and scalable, allowing the synthesis of highly stable NPs without additional capping agents [6]. Pros and cons of EPD of preformed NPs will be highlighted in comparison with the direct reduction of gold precursors on SiNW surface. The role of silicon doping will be investigated in combination with the charge of AuNP surface, to evaluate their influence on final material properties. To this aim, the results obtained on their electrochemical, spectroscopic and morphological characterizations will be presented.

[1] C. D’Andrea, M.J. Lo Faro, G. Bertino, P.M. Ossi, F. Neri, S. Trusso, P. Musumeci, M. Galli, N. Cioffi, A. Irrera, F. Priolo, B. Fazio, *Nanotechnology* **2016**, 27, 375603.
[2] R.A. Picca, C.D. Calvano, M.J Lo Faro, B. Fazio, S. Trusso, P.M. Ossi, F. Neri, C. D’Andrea, A. Irrera, N. Cioffi, *J. Mass Spectrom.* **2016**, 51, 849.
[3] M. Casiello, R.A. Picca, C. Fusco, L. D’Accolti, A.A. Leonardi, M.J. Lo Faro, A. Irrera, S. Trusso, P. Cotugno, M.C. Sportelli, N. Cioffi, A. Nacci, *Nanomaterials* **2018**, 8, 78.
[4] A. Irrera, M.J. Lo Faro, C. D’Andrea, A.A. Leonardi, P. Artoni, B. Fazio, R.A. Picca, N. Cioffi, S. Trusso, G. Franzò, P. Musumeci, F. Priolo, F. Iacona, *Semicond. Sci. Technol.* **2017**, 32, 043004.
[5] M. Izzi, M. C. Sportelli, L. Tursellino, G. Palazzo, R. A. Picca, N. Cioffi, Á.I. López Lorente, *Nanomaterials* **2020**, 10, 622.
[6] Á.I. López-Lorente, B.M. Simonet, M. Valcárcel, S. Eppler, R. Schindl, C. Kranz, B. Mizaikoff, *Talanta* **2014**, 118, 321.

Using TXM and 2D-XRF for the identification of inhomogeneous state of charge in Manganese Hexacyanoferrate Cathode Material

Mariam Maisuradze[a] *, Min Li*[a]*, Angelo Mullaliu*[b,c]*, Andrea Sorrentino*[d]*, Dino Tonti*[e]*, Ilaria Carlomagno*[f]*, Giuliana Aquilanti*[f]*, Jasper Rikkert Plaisier*[f]*, Stefano Passerini*[b,c]*, and Marco Giorgetti*[a]

[a]*Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale del Risorgimento 4, 40136 Bologna Italy;* [b]*Helmholtz Institute Ulm (HIU), Helmholtzstrasse 11, 89081, Ulm, Germany;* [c]*Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021 Karlsruhe, Germany;* [d]*ALBA Synchrotron Light Source, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallés, Spain;* [e]*Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC), Campus UAB Bellaterra, 08193 Cerdanyola del Vallès, Spain;* [f]*ELETTRA Sincrotrone Trieste S.C.p.A., Elettra - Sincrotrone Trieste S.C.p.A., 34149 Trieste, Basovizza, Italy.*

Energy-dependent full field transmission soft X-ray microscopy (TXM) is able to give a full picture at the nanometre scale of the chemical state and spatial distribution of the elements inside material. In a synchrotron-based TXM the spatial resolution for chemical information is few tens of nanometers. By using X-rays of the "soft" energy region (<3 KeV), it is possible to access transitions from core levels of light elements, such as the K-edge of nitrogen, oxygen, fluorine, as well as L – and M - edges of heavier elements [1, 2]. TXM provides pixel-by-pixel absorption spectrum, making it possible to select groups of pixels and map regions with the similar spectral features. Distributions of thickness, as well as absorption artifacts can also be investigated [3].
Complementary to TXM, another powerful analytical tool, 2D XRF (X-ray fluorescence) analysis was used, which is able of the spectrochemical determination of almost every element. In this case, the machine was equipped with hard X-ray source, which generally gives the opportunity to identify Z>8 elements [4]. The source in 2D-XRF machine is re-imaged to a 450 x 300 μm beamsize at exit slits [5], consequently, the obtained image is representative for the whole sample, whereas, TXM, with routinely expected spatial resolution of 30 nm in 2D, is probing a portion of the sample only.
The capabilities of both of those techniques as well as their complementarity was evident in our studies of characterization of cathode material, namely manganese hexacyanoferrate (MnHCF). It has open framework structure, redox-active sites and strong structural stability. High specific capacity of MnHCF and redox plateaus at high voltage are favourable qualities as an electrode material [6]. Spectromicroscopical studies were useful to observe inhomogeneous state of charge within the MnHCF electrode after cycling. In TXM the peak intensity ratios and in 2D-XRF tuning the incident energy of the beam showed different contribution of the charge species within the samples. Intercalation has been found in the peripheries of fully charged samples after 20 cycle in 2D XRF analysis and randomly distributed intercalated regions after 50 cycles in TXM analysis.

[1] D. Tonti, M. Olivares-Marín, A. Sorrentino, E. Pereiro, L. P. Mehdi Khodaei, Ed., IntechOpen, 22 March, 2017.

[2] D. Attwood, Cambridge: Cambridge University Press, 1999.

[3] A. Sorrentino, L. Simonelli, A. Kazzazi, N. Laszczynski, A. Birrozzi, A. Mullaliu, E. Pereiro, S. Passerini, M. Giorgetti, D. Tonti, *Applied Sciences,* no. 11, p. 2791, 2021.

[4] E. Margui, R. V. Grieken, New York, Momentum Press, 2013.

[5] "X-ray Fluorescence: Specifications," Elettra Synchrotron Trieste, 31 July 2019. [Online].

[6] A. Mullaliu, J. Asenbauer, G. Aquilanti, S. Passerini, M. Giorgetti, *Small Methods 4,* p. 1900529, 2020.

Analytical characterization of industrial substrates modified with antimicrobial metal nanoparticles for automotive applications

*Maria Chiara Sportelli [a], Margherita Izzi [a], Rosaria Anna Picca [a], Nicola Cioffi [a]**

[a] *Chemistry Department, University of Bari Aldo Moro, via E. Orabona 4, 70126 Bari, Italy*

Industrial substrates like leather, leatherette, polycarbonate, polyurethane, etc., modified by coatings implementing metal nanoparticles (MeNPs) represent one of the outcomes of the Italian MIUR project "E-Design" ARS01_01158 we carried out in the last two years. These antimicrobial materials were successfully applied as a key-component of several industrial goods for automotive industry. However, the widespread use of nanomaterials in commercial goods poses some concerns regarding human and environmental health. As a result, a detailed characterization of NP-treated materials is unavoidable [1]. Here we present the most representative results of the analytical characterization of these composite materials in terms of morphology, surface chemical composition, ionic release in contact media. Scanning Electron Microscopy (SEM) was used to assess the composite morphology. X-ray Photoelectron Spectroscopy (XPS) provided quantitative information about metal surface availability, and metals surface chemical state was evaluated by means of their main Auger signal. Electro-Thermal Atomic Absorption Spectroscopy allowed investigating metal ion release in contact media such as physiological solutions. The potential release of entire nanoparticles from treated materials was studied by Transmission Electron Microscopy (TEM) on contact solutions, aimed at ruling out or quantifying the extent of whole particle release under real-life usage conditions. Conclusions will be drawn about the safety and efficiency of the mentioned composites.

Acknowledgements:
Partial financial support is acknowledged from the European Union, PON Research and Innovation 2014-2020 – Project: "E-Design. Combinazione di design, elettronica e materiali multifunzionali per nuovi componenti estetici" ARS01_01158.

References:

[1] M.C. Sportelli et al., *Nanomaterials*, **2017**, 7, 203.

Advancements in sample preparation for performing elemental analysis of human hair by inductively coupled plasma mass spectrometry

Maria Luisa Astolfi[a], Francesca Sebastiani[a], Flavia Mancini[a], C. Mazzei[b], S. Canepari[c], G. Pietris[d]

[a] Department of Chemistry, Sapienza University, Piazzale Aldo Moro 5, I-00185 Rome, Italy; [b] Canon Toshiba Medical Systems s.r.l., Via Canton 115, I-00144 Rome, Italy; [c] Department of Environmental Biology, Sapienza University, Piazzale Aldo Moro 5, I-00185 Rome, Italy; [d] Department of General Surgery, Thoracic Diseases General Hospital Sotiria of Athens, Mesogion 152, 115 27 Athens, Greece

The determination of minerals and trace elements in human hair is potentially useful for assessing an individual's health status and monitoring occupational and environmental exposure [1,2,3]. Moreover, human hair is a stable matrix that presents numerous advantages for human biomonitoring, such as easy collection, low cost, easy transport and storage, and information about short- and long-term exposure. Consequently, its use in toxicological, clinical, environmental, and forensic investigations is growing and becoming more extensive. On the other hand, owing to the lack of standardized hair analysis procedures (including sample treatment methods), it is difficult to compare and interpret the results (intervals and reference values) from different studies and reach significant conclusions. In particular, recent reviews have revealed that analytical characteristics (detection/quantification limits and accuracy) are scarcely reported. Analyte loss, contamination, and/or interferences may also lead to a decrease in the analytical accuracy of the results. Incomplete decomposition of the hair samples involves an appreciable amount of residual carbon (C) in the resulting sample solution. In inductively coupled plasma spectrometry (ICP) techniques, this leads to the increased signal of some elements by carbon charge transfer reactions, especially for elements that have similar ionization potentials to that of C [4]. Another source of error in hair analysis by ICP with mass spectrometry (ICP-MS) is the interference caused by the residual acidity in the digests, difference between the viscosity and acid concentrations of the calibration and sample solutions, and the presence of polyatomic ions in the plasma [4]. Considering these aspects, the aim of this study was to optimize and validate a fast screening analytical method for the determination of 40 elements (Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, U, V, W, Zn, and Zr) in small-size (0.02 g) human hair specimens. The samples were subjected to HNO_3/H_2O_2 (2:1) digestion in an open vessel heated in a water bath and subsequently analyzed by ICP-MS equipped with a collision-reaction interface [4]. This method was used to determine the levels of essential and toxic heavy metals in the hair of children living in the Benishangul-Gumuz region, a Developing Regional State of North-Western Ethiopia [1]. The influence of several factors in the variability of element concentrations in children's hair (age, sex, body mass index, passive smoking, and eating habits) was also studied [1].

.

.

[1] M.L. Astolfi, G. Pietris, C. Mazzei, E. Marconi, S. Canepari, *Int. J. Env. Res. Pub. He.* **2020,** *17,* 8652.

[2] M.L. Astolfi, C. Protano, E. Marconi, L. Massimi, D. Piamonti, M. Brunori, M. Vitali, S. Canepari, *Int. J. Env. Res. Pub. He.* **2020,** *17*, 1911.

[3] C. Protano, M.L. Astolfi, E. Marconi, A. Antonucci, S. Canepari, D. Piamonti, M. Brunori, M. Vitali, Biol. Trace Elem. Res. **2020,** *197*, 89–100.

[4] M.L. Astolfi, C. Protano, E. Marconi, L. Massimi, M. Brunori, D. Piamonti, G. Migliara, M. Vitali, S. Canepari, Anal. Methods **2020,** *12*, 1906–1918.

REEs exposure and related toxicity to car repair workers

A. A. Brouziotis [a,b], G. Pagano [b,c], A. Giarra [b], M. Toscanesi [b], A. Di Nunzio [b], F. Lombardo [b,c], G. Libralato [a], M. Guida [a,c], M. Trifuoggi [b,c]

[a] *Department of Biology, University of Naples Federico II, Complesso Universitario di Monte Sant'Angelo, Via Cinthia 21, 80126 Naples, Italy*

[b] *Department of Chemical Sciences, University of Naples Federico II, Complesso Universitario di Monte Sant'Angelo, Via Cinthia 21, 80126 Naples, Italy*

[c] *Centro Servizi Metrologici e Tecnologici Avanzati (CeSMA), Complesso Universitario di Monte Sant'Angelo, Via Cinthia 21, 80126 Naples, Italy*

Rare earth elements (REEs) have become an essential component of present-day life due to their pervasive applications in several industrial, agricultural and medical applications. Thus, one has to recognize the indispensable roles that REEs have acquired in the present world. This extensive use of REEs in a number of technologies is expected to impact human health, including occupational and environmental REE exposures. A body of experimental evidence on REE-associated toxicity in a number of biota, including mammals (both in vivo and in vitro models), other vertebrates, invertebrates, and plant and microbial models has been accumulated in recent decades, providing extensive background information on the adverse effects of REE exposures [1].

Unlike experimental studies, the consequences of REE exposures to human health have been subjected to relatively fewer investigations. The likely environmental threats arising from REE exposures deserve a new line of research efforts [2]. Environmental exposures have been biomonitored in populations residing in REE mining areas, showing REE bioaccumulation in scalp hair, excess REE urine levels, and defective gene expression [2,3].

Some REE occupational exposures, in jobs such as glass polishers, photoengravers and movie projectionists showed a few case reports on health effects affecting the respiratory system [3]. As for other REE occupational exposures, mention should be given to jobs within e-waste processing and, diesel engine repair and maintenance, with exposures to exhaust microparticulate (containing nanoCeO2 as a catalytic additive). Diesel exhaust microparticulate has been studied in animal models, leading to evidence of several pathological effects in animals exposed by respiratory or systemic routes. The current experimental evidence for REE-associated toxicity raises environmental health concern on the possible adverse effects in areas affected by excess REE pollution, such as close to mining areas or related to REE manufacturing [1].

To establish a safe and healthy working environment for REE industries, the use of biomarkers is increasing to provide sustainable measure, due to demand for information about the health risks from unfavorable exposures. Given the recent toxicological results on the exposure of cells, animals and workers to REE compounds, it is important to improve the current understanding of the REE compounds in the field of occupational health. This will help to establish a sustainable, safe and healthy working environment for REE industries [4].

In this study, in collaboration with the local sanitary institution of Avellino (A.S.L.), we evaluated for the very first time, the levels of REEs in urine of mechanics that are engaged in the maintenance and repair of diesel engines. The focus is on workers in the car repair sector, where the risk of inhalation of emissions from combustion products richer in REEs is potentially more likely. We also wished to evaluate the correlation between the levels of 1-hydroxypyrene and exposure to REEs. We elaborated two different methods to investigate the effectiveness, one by simple dilution with HNO_3 and the other by doing a microwave assisted-acid digestion. The analysis of the content was elaborated by using the ICP-MS technique.

References

[1] G. Pagano, J. P. Thomas, A. Di Nunzio, M. Trifuoggi, 2019. Human exposures to rare earth elements: Present knowledge and research prospects. Environmental Research, 171, 493-500

[2] G. Pagano, M. Guida, F. Tommasi, R. Oral, 2015. Health effects and toxicity mechanisms of rare earth elements – Knowledge gaps and research prospects. Ecotoxicology and Environmental Safety, 115, 40-48

[3] G. Pagano, F. Aliberti, M. Guida, R. Oral, A. Siciliano, M. Trifuoggi, F. Tommasi, 2015. Rare earth elements in human and animal health: State of art and research priorities. Environmental Research, 142, 215-220

[4] K. T. Rim, K. H. Koo, J. S. Park, 2013. Toxicological evaluations of rare earths and their health impacts to workers: A literature review. Safety and Health at Work, 4(1), 12-26

Skin absorption of metals following exposure to road dust powder

*Greta Camilla Magnano [a] *, Giovanna Marussi [b], Elena Pavoni [c], Gianpiero Adami [b], Francesca Larese Filon [a] , Matteo Crosera [b]*

[a] Clinical Unit of Occupational Medicine, University of Trieste, Italy; [b] Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy; [c] Department of Mathematics and Geosciences, University of Trieste, Italy

Human skin forms a unique interface between the body and the external environment. Its main role is to protect the internal organs from external factors. Notably, the outermost skin layer, *stratum corneum*, forms a remarkable barrier for permeation of xenobiotics in general, but unfortunately it may become an entry route of hazardous substances. Metals can penetrate and permeate the skin inducing local effects such as skin sensitization with allergic contact dermatitis and potential metals diffusion into the bloodstream with systemic intoxication[1] [2].
Metals in nano dimensions penetrate and permeate the skin in higher amount[3] [4] compared to bulk materials due to their smaller dimensions[5].Therefore, if the *stratum corneum* is damaged to various factors such as inflammation, desquamation, defects in lipid distribution or epidermal thickening, the transcutaneous passage of a molecule is expected to be drastically enhanced[6] [7]. In this study, we investigate the percutaneous penetration of metals from the road dust powder in intact as well damaged skin to mimic the effect of skin lesions. In addition, porcine and human skin were compared as skin models. The certified reference material BCR®-723 provided by the European Institute for Reference Materials and Measurements was used as road dust formulation. To evaluate the extent of ionization of metals from BCR®-723, the dissolution of powder in synthetic sweat solutions at two different pH (pH 4.5, 6.5) was carried out. Periodic quantification of metals concentration was monitored and analyzed via inductively coupled plasma - optical emission spectroscopy (ICP-OES). The choice of synthetic sweat solution at pH 4.5 was dictated to reproduce the workplace conditions. Dermal absorption from donor compartment containing metals was monitored for 24 hours. The amounts of metals retained in skin were quantified post-exposure by inductively coupled plasma - mass spectrometer (ICP-MS). Percutaneous absorption of lead (Pb) was higher in both intact skin models (549 ng/cm^2 in porcine skin *vs* 68.80 ng/cm^2 in human model). Moreover, cobalt (Co) accumulation was higher in porcine skin reaching a value of 518 ng/cm^2 than those found in human skin (1.85 ng/cm^2). In contrast with the observations reported in human skin model, chromium (Cr) achieved the lowest skin absorption in porcine model (183 ng/cm^2). As expected, metals permeation on damaged skin was enhanced due to the removal of the barrier function. These consequence differences may be due to the skin tissues, but pig skin appeared as the most suitable replacement for human skin.

[1] M. Crosera, *et al.*, *Chemosphere*, **2016**, 145, 301-306.
[2] F.L.Filon, et al., *Toxicology in Vitro*, **2009**, 23, 574-579.
[3] F.Larese Filon, *et al.*,*International Journal of Hygiene and Environmental Health*, **2016**, 219, 536-544.
[4] D.H.Brouwer *et al.*, *International Journal of Hygiene and Environmental Health*, **2016**, 219, 503-512.
[5]F.Larese Filon *et al.*, *Regulatory Toxicology and Pharmacology*, **2015**,72, 310-322.
[6]S. Kezic, J. B. Nielsen, *International Archives of Occupational and Environmental Health*, **2009**, 82, 677-688.
[7]J. B. Nielsen, *Archives of Dermatological Research*, **2005,** 296, 560-567.

Oral fluid as a new investigative matrix to assestment OGSR exposure

Flavia Pagano[a,b], Flaminia Vincenti[a,b], Camilla Montesano[b], Adolfo Gregori[c], Roberta Curini[b], Manuel Sergi[d]

[a] *Department of Public Health and Infectious Disease, Sapienza University of Rome, Rome, Italy*
[b] *Department of Chemistry, Sapienza University of Rome, Rome, Italy*
[c] *Carabinieri, Department of Scientific Investigation, Rome, Italy*
[d] *Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Teramo, Italy*

In recent years, increased usage of ammunition without lead and heavy metals was observed, from which it derives a growing interest in the detection of organic gunshot residues (OGSR) as firearms related crimes evidences. The wide range of compounds belonging to OGSR class has proven to be challenging as different ionization techniques may be needed to obtain good results for all compounds.

Gas chromatography coupled with mass spectrometry (GC-MS) was used extensively for OGSR determination. The analysis of OGSR by LC-MS is not straightforward, especially because of their limited ionization efficiency; the use of atmospheric pressure chemical ionization (APCI) source operating in negative mode is often reported while only a few references report the use of an Electrospray source (ESI). In addition, to the best of our knowledge, the determination of both OGSR and stabilizers in a single chromatographic run has never been reported.

Due to the growing interest in the determination of OGSR, the purpose of this work is to develop and validate an analytical method for the determination of the most common explosives and the most used stabilizers, coming from both residues from Fire Discharge Residues and post-deflagration in oral fluids (OF) by means of UHPLC-HRMS; it could be a suitable and reliable tool for law enforcement authorities for the detection of explosives in forensic potential scenarios, including biological matrices.

In this study, SPE was used for the cleanup of OF before UHPLC-HRMS analysis. This extraction technique has demonstrated to be suitable for OF. Thanks to the coupling of high-performance liquid chromatography with high resolution mass spectrometry (UHPLC-HRMS) it was possible to develop an innovative method for the simultaneous analysis of the most common OGSR and the four most used stabilizers in OF. The 13 compounds were chromatographically separated by means of a Polar-C18 column. A chlorinated compound was added to the mobile phases in order to promote the formation of chloride adduct ions. The ion source used in this work was an H-ESI operating in polarity switching to allow the best conditions for each analyte. The detection was conducted with a high-resolution mass spectrometer with Orbitrap technology in Full scan/data dependent acquisition mode, in order to detect both of the precursor ions and as concern stabilizers also the most intense fragments. To verify the applicability of the method, it was applied to some real samples. A shooting session was performed in an open shooting range. The shooters fired from 2 to 200 rounds with a cal. 9x21IMI, after which they were sampled. Samples were analyzed confirming that explosives may be detected in OF, the use of this matrix may be of great interest for investigative purposes as it is not affected by secondary transfer.

[1] D. Perret, S. Marchese, A. Gentili, R. Curini, A. Terracciano, E. Bafile, F. Romolo, *"LC– MS–MS Determinatin of Stabilizers and Explosives Residues in Hand-Swabs"*, Chromatographia **2008**, 68, 517–524

[2] X. Xu, A. M. vande Craats, P. C.A.M. de Bruyn, *"Highly sensitive screening method for nitroaromatic, nitramine and nitrate ester explosives by high performance liquid chromatography-atmospheric pressure*

ionization-mass spectrometry (HPLC-API-MS) in forensic applications", J. Forensic Sci. **2004**, 49, 6, 1171–1180

[3] J. L. Thomas, D. L., "*Separation and Detection of Smokeless Powder Additives by Ultra Performance Liquid Chromatography with Tandem Mass Spectrometry (UPLC/MS/MS)*", Journal of Forensic Sciences **2013**, 58 (3), 609–615

[4] S. C. Bell, M. Gayton-Ely, C M. Nida, "*Bioassays for bomb-makers: proof of concept*", Anal Bioanal Chem **2009,**395:401–409

Forensic skin proteomics towards wound age estimation

Lorenzo Toma[a], Monica Mattarozzi[a], Stefano Bruno[b], Simona Nonnis[c], Gabriella Tedeschi[c], Marco Milioli[d], Giulia Vignali[e], Cristina Cattaneo[e], Maria Careri[a]

[a] Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Italy; [b] Department of Food and Drug, University of Parma, Italy; [c] Veterinary Medicine Department (DIMEVET), University of Milan, Italy; [d] Department of Pharmacokinetic, Biochemistry and Metabolism, Preclinical Area, Chiesi Farmaceutici SpA, Parma, Italy; [e] Legal Medicine Institute, Department of Biomedical Sciences for Health, University of Milan, Italy

Mass spectrometry (MS)-based proteomics has recently attracted the attention of forensic scientists and pathologists owing to its potential to answer different forensic questions and strengthen scientific evidence for legal cases [1]. In particular, differential proteomics of biological samples under different physiological states could help identify new biomarkers. In this context, the assessment of the lapse time between injuries and death is a well-known issue in pathology, but it is still relatively unexplored with proteomic approaches [2].

The present study focused on the development of a proteomic-based analytical approach for wound age estimation in autoptic skin human samples as an alternative to traditional immunohistochemical assays. Among all wound types, ecchymoses were selected since they are vital by definition. The analytical protocol developed consisted of a pulverization step followed by defatting and protein extraction under denaturing conditions by bead beating. Then, the total protein content was quantified and proteins were digested with trypsin. The resulting peptides were finally purified with a C18 ZipTip prior to liquid chromatography-high resolution mass spectrometry (LC-HRMS) analysis. At first, 12 couples (ecchymosis and normal tissues) of skin samples were collected. For each sample type, extracts were randomly combined to obtain two different pools. In order to assess the reproducibility of the analytical approach, two independent replicates for each sample were performed within four months. About 2000 proteins were identified in each skin sample with reproducibility values higher than 93% for independent replicates in terms of total proteins. It was possible to identify twelve proteins unique to the ecchymotic tissues, which could represent new biomarkers of ecchymosis, possibly related to wound age. These proteins are involved in immune responses, in the complement system, and in the coagulation cascade. The confirmation of their potential use as biomarkers will require an in-depth study. The analysis of additional samples and the collection of characterized samples in terms of wound age are currently in progress.

[1] V.-A. Duong, J.-M. Park, H.-J. Lim, H. Lee, *Appl. Sci.* **2021**, *11*, 3393.
[2] C. Cattaneo, S. Andreola, E. Marinelli, P. Poppa, D. Porta, M. Grandi M, *Am. J. Forensic Med. Pathol.* **2010**, *31*, 22.

Determination of Total Hydroxytyrosol and Tyrosol in Extra Virgin Olive Oils by using a Natural Deep Eutectic Solvent

Francesco Longobardi [a], Vito Michele Paradiso [b,c], Stefania Fortunato [c], Pasqua Rotondi [a], Maria Bellumori [d], Lorenzo Cecchi [d], Pinalysa Cosma [a], Nadia Mulinacci [d], and Francesco Caponio [c]

[a]Department of Chemistry, University of Bari, Via Orabona 4, I-70126, Bari (Italy);
[b]Department of Biological and and Environmental Sciences and Technologies, University of Salento, I-73100, Lecce (Italy);
[c]Department of Soil, Plant and Food Sciences, University of Bari, Via Amendola 165/a, I-70126, Bari (Italy);
[d]Department of NEUROFARBA, and Multidisciplinary Centre of Research on Food Sciences (M.C.R.F.S.-Ce.R.A.), University of Firenze, Via Ugo Schiff 6, I-50019 Sesto F.no (Firenze), Italy;

The European Food Safety Authority (EFSA) allowed a health claim for labelling olive oils containing a minimum amount of hydroxytyrosol (OHTyr) and its derivatives, including tyrosol (Tyr). Therefore, analytical protocols are required in support of an effective application of the health claim. In this work, a natural deep eutectic solvent was used to perform a liquid/liquid extraction of phenolic compounds from extra virgin olive oil samples, followed by UV-spectrophotometric analysis. The spectral features of the extracts were related with the content of total OHTyr and Tyr, determined by an acid hydrolysis-chromatographic method [1]. Three single wavelengths of the second derivative of spectra (i.e., 299 nm, 290 nm, and 282 nm) significantly related with total OHTyr, total Tyr, and their sum, respectively. In particular, the sum of OHTyr and Tyr could be determined with a root mean square error of prediction of 29.5 mg kg-1, while the limits of quantitation and detection were respectively 11.8 and 4.9 mg kg-1. The proposed method [2], therefore, represents an fast, green, and easy method useful for on-site screening and monitoring applications.

[1] M. Bellumori, L. Cecchi, M. Innocenti, M.L. Clodoveo, F. Corbo, N. Mulinacci, *Molecules*, **2019**, 24, 2179.
[2] V.M. Paradiso, F. Longobardi, S. Fortunato, P. Rotondi, M. Bellumori, L. Cecchi, P. Cosma, N. Mulinacci, F. Caponio, *Foods*, **2021**, 10, 677.

INDICE COMUNICAZIONI ORALI

Astolfi	Paola	TEC OR042
Atzori	Matteo	INO OR025
Audisio	Davide	ORG OR003
Avola	Tiziana	ANA OR086
Ayaz	Nazeeha	TEC OR027
Aye	Yimon	FAR KN005
Bacchiocchi	Riccardo	IND OR058
Baccolo	Giacomo	ANA OR034
Bach	Anders	FAR KN009
Badetti	Elena	ABC OR007
Baglio	Vincenzo	ELE OR57
Baglioni	Michele	FIS OR076
Baldassarre	Francesca	TEC OR041
Baldelli	Francesca	FIS OR067
Baldini	Laura	ORG OR087
Ballarotto	Marco	ORG OR019
Balliana	Eleonora	ABC OR002
Balsamo	Stefano Andrea	IND OR047
Bandiera	Tiziano	FAR KN011
Baratta	Mariafrancesca	FIS OR107
Barbanente	Alessandra	INO PZ008
Barbera	Vincenzina	TEC OR021
Barberis	Elettra	MAS OR005
Barbieri	Luisa	ABC OR054
Barbieri	Pierluigi	ABC OR058
Bardi	Brunella	FIS OR103
Barlocco	Ilaria	INO OR002
Barola	Carolina	MAS OR011
Baron	Marco	INO OR019
Barone	Laura	ANA OR114
Barreca	Marilia	FAR OR011
Bartella	Lucia	MAS OR010
Battista	Sara	ORG OR004
Battistuzzi	Gianantonio	CSB OR003
Begni	Federico	FIS OR088
Bella	Federico	IND OR036
Bellassai	Noemi	ANA OR068
Bellavita	Rosa	FAR OR042
Bellia	Francesco	CSB OR022
Bellina	Fabio	ORG OR069
Bellini	Marco	INO OR041
Belloni	Alessia	INO OR048
Bellotti	Denise	ANA OR087
Bellotto	Ottavia	CSB OR002
Benedetti	Michele	INO OR008
Bernardi	Anna	ORG PZ001
Bernes	Elisa	TEO OR017
Bernini	Roberta	ORG OR005
Bertani	Marco	TEO OR001
Bertinetti	Stefano	ANA OR060
Berto	Silvia	ANA KN010

Bertucci	Alessandro	ANA OR069
Bertuletti	Susanna	ORG OR117
Bertuzzi	Giulio	ORG OR108
Bettini	Simona	FIS OR080
Biagini	Denise	ANA OR035
Biagiotti	Giacomo	ORG OR027
Bianchera	Annalisa	TFA OR010
Bianchi	Federica	ANA OR076
Bianco Prevot	Alessandra	ANA IL005
Biancolillo	Alessandra	ANA KN004
Biasi	Pierdomenico	IND KN003
Biesuz	Raffaela	ANA OR123
Biffis	Andrea	INO OR022
Bifulco	Aurelio	TEC OR017
Biggio	Deborah	ANA OR115
Bigogno	Alessandra	ABC OR006
Bisag	Denisa	ORG OR118
Biscaglia	Francesca	FIS OR064
Bizzarri	Bruno Mattia	ORG OR020
Blangetti	Nicola	FIS OR111
Blasi	Davide	ORG OR028
Bloise	Ermelinda	TEC OR004
Bogialli	Sara	MAS KN003
Boldrini	Chiara Liliana	ORG OR080
Bollella	Paolo	ANA KN009
Bolognesi	Margherita	FIS OR049
Bonacchi	Sara	ELE OR11
Bonaccorso	Angela	TFA OR002
Bonfio	Claudia	CSB PZ002
Bonini	Andrea	ANA OR017
Bonini	Mauro	TFA IL003
Bonizzoni	Simone	ELE OR53
Bonomo	Matteo	ELE KN34
Bonomo	Matteo	IND OR039
Borella	Matteo	IND OR064
Bortolato	Tommaso	ORG OR109
Bossi	Alberto	ORG OR029
Bossi	Alessandra Maria	ANA OR070
Botla	Vinayak.	IND OR010
Braconi	Laura	FAR OR012
Branchini	Federica	DID OR001
Brandi	Jessica	ANA OR095
Brandiele	Riccardo	ELE IL31
Bretti	Clemente	ANA KN002
Brilloni	Alessandro	ELE OR67
Brufani	Giulia	ORG OR119
Brugnoli	Luca	TEO OR006
Brunelli	Andrea	ABC OR015
Brunetti	Leonardo	FAR OR009
Brunsveld	Luc	CSB KN003
Budroni	Marcello	FIS OR122

Buonsenso	Fabio	ORG OR033
Busato	Matteo	FIS OR094
Buscemi	Gabriella	ORG OR081
Cabri	Walter	IND KN002
Cademartori	Davide	ELE OR56
Caflisch	Amedeo	CSB KN006
Calà	Elisa	ANA OR063
Calabrese	Carla	IND OR024
Calandra	Pietro	ABC OR055
Calandra	Pietro	FIS OR085
Calcaterra	Andrea	ORG OR006
Calcio Gaudino	Emanuela	ORG OR120
Calgaro	Loris	ABC OR056
Calogero	Francesco	ORG OR121
Calvano	Cosima Damiana	ANA IL004
Calvini	Rosalba	ANA OR132
Calvino	Martina Maria	FIS OR118
Campagnolo	Filippo	INO OR024
Campanella	Beatrice	ANA OR116
Campiani	Giuseppe	FAR KN001
Campisciano	Vincenzo	ORG OR122
Campisi	Sebastiano	FIS OR034
Campisi	Sebastiano	IND OR014
Campitelli	Patrizio	INO OR037
Cannavacciuolo	Ciro	MAS OR009
Capone	Matteo	TEO OR015
Cappai	Rosita	ANA OR088
Caprioglio	Diego	ORG OR021
Capriotti	Anna Laura	ANA IL009
Caputo	Paolino	FIS OR040
Cara	Claudio	FIS OR105
Caratelli	Veronica	ANA OR134
Carbone	Daniela	FAR OR013
Cardoso Gomes	Guelber	TEO OR016
Carena	Luca	ANA OR061
Carmignani	Alessio	FIS OR099
Carpanese	Maria Paola	ELE OR48
Carpentieri	Maria Antonietta	DID OR002
Carucci	Cristina	FIS OR063
Caruso	Manfredi	TEC OR005
Casini	Angela	CSB KN005
Castiglione	Franca	TEC OR010
Casula	Luca	TFA OR011
Cataldo	Salvatore	ANA OR089
Catani	Martina	ANA PZ004
Catelli	Emilio	ANA OR064
Catto	Marco	FAR OR031
Cavalera	Simone	ANA OR096
Cavazza	Antonella	ANA OR025
Cavuoto	Denise	IND OR002
Cecchi	Teresa	DID OR010

Cecconi	Daniela	MAS OR001
Ceccucci	Anita	TEC OR045
Cefali	Manuel Amedeo	ABC OR059
Centomo	Paolo	INO OR033
Cerrato	Andrea	ANA OR097
Cerri	Luca	TFA OR012
Cesari	Cristiana	INO OR035
Chelazzi	David	FIS OR 129
Chenet	Tatiana	ANA OR026
Chiarcos	Riccardo	IND OR027
Chiarello	GianLuca	FIS OR030
Chino	Marco	INO OR032
Chiodo	Fabrizio	ORG OR007
Chirizzi	Cristina	FIS OR081
Ciacci	Luca	ABC OR003
Ciccola	Alessandro	ABC OR008
Cinti	Stefano	ANA OR071
Cioffi	Nicola	ANA IL010
Cipriano	Domenico	ABC OR045
Cirillo	Martina	ORG OR008
Clemente	Ilaria	FIS OR065
Cleto Bruzzese	Paolo	INO OR027
Colella	Marco	ORG OR022
Colella	Maria Francesca	FIS OR115
Collini	Elisabetta	FIS OR047
Colloca	Stefano	TFA IL002
Colozza	Noemi	ANA OR135
Comis	Silvia	ELE OR43
Condorelli	Marcello	FIS OR009
Consentino	Luca	IND OR015
Conte	Francesco	IND OR045
Contente	Martina	FAR OR018
Conti	Luca	INO OR023
Coralli	Irene	ANA OR077
Corbisiero	Dario	ORG OR023
Cordaro	Massimiliano	ORG OR024
Corinti	Davide	INO OR063
Corno	Marta	FIS OR101
Corradini	Danilo	ANA OR024
Corrente	Giuseppina Anna	FIS OR035
Corrieri	Matteo	ORG OR132
Cosentino	Ugo	DID OR015
Costa	Maria	DID OR003
Costanzo	Paola	ORG OR061
Cozzolino	Antonietta	IND OR028
Cristiano	Maria Chiara	TFA OR013
Cristina	Tealdi	ELE KN68
Crivellaro	Giovanni	ELE OR07
Crocetti	Letizia	FAR OR006
Cucinotta	Lorenzo	ANA OR003
Cupellini	Lorenzo	TEO PZ005

Curti	Claudio	ORG OR059
D’Ambrosio	Valeria	ABC OR022
D’Imperio	Nicolas	ORG PZ012
Da Pian	Marta	ORG OR034
D’Agata	Roberta	ANA OR117
Dai	Yasi	TEO OR018
Dal Bello	Federica	ANA OR028
Dall’Anese	Anna	INO PZ002
D’Alterio	Massimo Christian	INO OR004
D’Amato	Alfonsina	ANA OR105
Damiano	Caterina	INO OR016
Damin	Alessandro	FIS OR126
Danielis	Maila	IND OR005
D’Aria	Federica	FIS OR018
Darjazi	Hamideh	ELE OR72
Davighi	Maria Giulia	ORG OR010
de Araujo Lima e Souza	Giselle	TEC OR011
De Bon	Francesco	ELE OR16
De Bonis	Angela	FIS OR097
De Castro	Cristina	ORG OR011
De Ceglie	Cristina	ABC OR017
De Filpo	Giovanni	FIS OR082
De Gennaro	Gianluigi	ABC OR001
De Grazia	Gemma	ANA OR004
De Leo	Vincenzo	FIS OR019
De Luca	Chiara	ANA OR106
De Marchi	Fabiola	MAS OR008
De Santis	Roberto	FIS KN012
De Santis	Serena	TEC KN003
De Zotti	Marta	CSB OR001
Deganello	Francesca	INO OR039
Degli Esposti	Lorenzo	FIS OR021
Del Coco	Laura	INO OR061
Del Galdo	Sara	TEO OR022
Del Giudice	Alessandra	FIS OR053
Del Giudice	Daniele	ORG OR088
Del Grosso	Erica	ANA OR072
Della Pelle	Flavio	ANA KN011
Dell’Edera	Massimo	FIS OR113
Deng	Siyuan	TFA OR009
Desantis	Jenny	ORG OR012
Dettin	Monica	FIS OR096
Di Capua	Angela	ANA OR098
Di Carlo	Gabriella	FIS KN010
Di Carluccio	Cristina	ORG OR013
Di Carmine	Graziano	ORG OR035
Di Donato	Francesca	ANA OR036
Di Fidio	Nicola	IND OR053
Di Giulio	Tiziano	ANA OR018
Di Guida	Rossella	ORG OR014
Di Liberto	Giovanni	FIS OR028

Di Liberto	Giovanni	TEO PZ003
Di Maiolo	Francesco	TEO OR029
Di Maro	Mattia	ORG OR110
Di Maro	Salvatore	FAR OR039
Di Matteo	Paola	TEC OR025
Di Muzio	Simone	FIS OR071
Di Nardo	Fabio	ANA OR099
Di Noja	Simone	ORG OR031
Di Pietro	Maria Enrica	TEC OR012
Di Porzio	Anna	CSB OR029
Di Terlizzi	Lorenzo	ORG OR063
Dibenedetto	Carlo Nazzareno	FIS OR001
Dichiara	Maria	FAR OR021
Dichiarante	Valentina	TEC OR031
Dilonardo	Elena	TEC OR028
Dini	Danilo	ELE OR17
Dispenza	Clelia	TEC OR046
Distefano	Alessia	CSB OR009
Dogra	Raghav	ANA OR009
Domestici	Chiara	INO OR042
Donà	Lorenzo	TEO OR030
Donati	Greta	TEO PZ001
Donato	Paola Agata	ANA OR030
Donnarumma	Danilo	ANA OR118
Donnoli	Maria Irene	DID OR011
D’Onofrio	Mariapina	ORG OR009
Dozzi	Maria Vittoria	FIS KN009
D’Urso	Alessandro	CSB OR010
Econdi	Stefano	IND OR011
El Fadil	Dounia	ANA OR107
Elbaz	Lior	ELE KN55
Elkhanoufi	Sabrina	CSB OR008
Elliani	Rosangela	ANA OR005
Erba	Alessandro	TEO PZ002
Ermini	Elena	ORG OR036
Escolano Casado	Guillermo	FIS OR069
Esposito	Anna	ORG PZ014
Esposito	Germana	ORG OR037
Esposito	Roberto	INO OR020
Esposito	Rodolfo	FIS OR106
Esposito	Tiziana	TFA OR014
Espro	Claudia	TEC KN001
Estima Gomes	Manuela	TFA IL005
Fabbiani	Marco	FIS OR006
fabbri	Debora	ANA OR029
Fabiani	Laura	ANA OR019
Facchetti	Giorgio	INO OR031
Facchin	Alessandro	ELE OR35
Facchin	Alessandro	ELE OR51
Faginas-Lago	Noelia	TEO OR008
Fagiolari	Lucia	IND OR061

Fagnani	Francesco	INO OR007
Falco	Marisa	ELE OR62
Falletta	Ermelinda	IND OR048
Famulari	Antonino	INO OR062
Fanizza	Elisabetta	FIS OR014
Fanti	Federico	MAS OR004
Fasano	Valerio	ORG OR116
Fasolini	Andrea	IND OR040
Fasulo	Francesca	TEO OR009
Fattal	Elias	TFA IL001
Federico	Bella	TEC OR038
Felletti	Simona	ANA OR078
Fenti	Angelo	ABC OR009
Ferdeghini	Claudio	ORG OR032
Ferdinando Summa	Francesco	TEO OR023
Ferlenghi	Francesca	FAR OR019
Fermi	Andrea	INO OR045
Fermo	Paola	ANA IL006
Feroci	Marta	ELE KN045
Ferracane	Antonio	ANA OR006
Ferrari	Giorgio	IND OR065
Ferraro	Giovanni	FIS OR011
Ferrauto	Giuseppe	INO OR051
Ferrazzano	Lucia	ORG OR064
Ferrero	Luca	ABC OR005
Ferretti	Francesco	INO OR021
Fidaleo	Marco	TFA IL004
Filippin	Ilaria	TFA OR003
Fiorentini	Carlo	DID IL002
Fiorentino	Antonino	ABC OR034
Fiorenza	Roberto	IND OR016
Fiorito	Daniele	ORG OR060
Fischer	Peter	ELE KN06
Forchetta	Mattia	ORG OR082
Fornari	Fabio	ANA OR037
Fornasier	Marco	FIS OR016
Forni	Alessandra	FIS OR044
Fortino	Mariagrazia	TEO OR010
Fortunati	Alessia	ELE OR21
Foschi	Francesca	ORG OR123
Francesconi	Oscar	ORG OR089
Franchina	Flavio	ANA KN001
Franchino	Allegra	ORG OR067
Franco	Francesca	ORG OR076
Franzini	Roberta	ORG OR038
Frateloreto	Federico	ORG OR133
Freccero	Riccardo	INO OR069
Frosi	Ilaria	FAR OR017
Froudakis	George	FIS KN007
Funicello	Maria	ORG OR015
Gabas	Fabio	FIS OR058

Gaeta	Massimiliano	CSB OR021
Gaggero	Elisa	ABC OR035
Gaggiotti	Sara	ANA OR124
Gagliardi	Anna	IND OR049
Galantini	Luciano	FIS KN011
Galassi	Rossana	INO OR047
Galeotti	Marco	ORG OR039
Galletta	Micaela	ANA OR007
Galloni	Melissa Greta	IND OR017
Gambassi	Francesca	INO OR049
Garbarino	Gabriella	IND OR006
García Lascurain	P. Guzmán	ABC OR046
Garello	Francesca	INO OR054
Gaspa	Silvia	ORG OR070
Gatti	Lucrezia	ABC OR028
Gatto	Emanuela	FIS KN003
Gazzola	Silvia	ORG OR138
Gazzotti	Stefano	IND OR023
Gelain	Arianna	FAR OR014
Gelli	Rita	FIS OR052
Geninatti	Simonetta	INO OR084
Gentile	Luigi	FIS KN004
Gentili	Dario	ORG OR016
Gentili	Pier Luigi	FIS OR038
Gessner	Viktoria	INO IL001
Ghedini	Elena	IND OR070
Ghini	Veronica	CSB OR006
Ghini	Veronica	INO OR070
Ghirga	Francesca	ORG OR041
Giacalone	Francesco	ORG PZ007
Giambastiani	Giuliano	IND OR063
Giannetto	Marco	ANA OR073
Giedroc	David	INO IL003
Gilda Ritacca	Alessandra	TEO OR020
Gioiello	Antimo	FAR KN006
Giordana	Alessia	INO OR030
Giorgi	Silvia	IND OR057
Giorno	Lidietta	CSB OR004
Giovanni	Falcone	TEC OR044
Giovannini	Tommaso	FIS OR060
Girlando	Alberto	FIS OR090
Girolametti	Federico	ANA OR010
Giuffrè	Ottavia	ANA OR090
Giuliano	Elena	TFA OR017
Giurlani	Walter	ANA OR119
Giustiniano	Mariateresa	FAR PZ002
Gobbo	Pierangelo	ORG PZ004
Gobetto	Roberto	INO OR001
Gois	Pedro	FAR KN012
Golla	Manohar	IND OR029
Goracci	Laura	ORG OR042

Laudadio	Gabriele	ORG PZ015
Laurati	Marco	FIS KN001
Laus	Michele	IND KN004
Lazzara	Giuseppe	ABC OR050
Leccese	Mirko	FIS OR102
Lenci	Elena	DID OR012
Lenci	Elena	ORG PZ009
Lenzi	Alessio	ANA OR108
Leonardo	Duranti	ELE OR49
Leone	Linda	INO OR005
Leonelli	Cristina	TEC OR016
Lesch	Andreas	ANA OR045
Li	Min	ANA OR121
Liccardo	Letizia	INO OR055
Licen	Sabina	ABC OR010
Licen	Sabina	ANA OR038
LiDestri	Giovanni	FIS OR002
Lipparini	Filippo	TEO OR025
Lippi	Martina	TEC OR033
Lisuzzo	Lorenzo	FIS OR072
Litti	Lucio	FIS OR078
Lo Porto	Chiara	FIS OR108
Lo Vecchio	Carmelo	ELE OR03
Locatelli	Marcello	ANA OR082
Lodesani	Federica	TEO OR031
Lodi	Giulia	ABC OR032
Loianno	Valerio	FIS OR086
Lombardi	Dora Stella	DID OR005
Lombardo	Marco	ORG OR135
Lopreside	Antonia	ANA OR074
Losi	Niccolo	ABC OR060
Lovison	Denise	INO OR056
Lucantonio	Stefania	IND OR060
Lucarini	Marco	ORG PZ005
Lucarini	Simone	FAR OR024
Lucenti	Elena	INO OR014
Lufrano	Ernestino	ELE OR65
Lunardon	Marco	INO OR072
Lupi	Michela	ORG OR136
Lupidi	Gabriele	ORG OR145
Luque	Rafael	IND KN006
M. Fiore	Ambra	TEC OR019
Maccarone	Giuseppina	MAS PL001
Macchia	Eleonora	ANA OR020
Magnaghi	Lisa Rita	ANA OR039
Magni	Mirko	ELE OR26
Mai	Antonello	FAR MD002
Maiuolo	Loredana	ORG OR074
Malacaria	Luana	ANA OR092
Malegori	Cristina	ANA KN005
Malferrari	Marco	ELE OR37

Malitesta	Cosimino	ANA OR136
Mameli	Valentina	FIS OR010
Manca	Gabriele	INO OR057
Mancinelli	Michele	ORG OR075
Mancini	Alessandro	ABC OR061
Manfredi	Marcello	ANA OR109
Manfredi	Norberto	ORG OR084
Mangini	Anna	ELE OR66
Mangraviti	Domenica	ANA OR051
Mannias	Giada	INO OR075
Mantovani	Marco	ABC OR020
Manzoli	Maela	IND OR051
Marasco	Daniela	INO OR060
Marassi	Valentina	ANA OR101
Marchesi	Stefano	FIS OR110
Marchiò	Luciano	INO OR077
Marcì	Giuseppe	TEC OR029
Marcolin	Giampaolo	FIS OR043
Maresca	Giovanna	ELE OR74
Maria Squeo	Benedetta	ORG OR106
Mariani	Federica	ANA OR021
Mariconda	Annaluisa	INO OR068
Mariotti	Nicole	IND OR032
Marittimo	Nicole	ANA OR052
Marotta	Angela	TEC OR009
Martella	Daniele	IND OR031
Martelli	Giulia	ORG OR137
Martina	Bortolami	TEC OR040
Martini	Francesca	FIS OR048
Martí-Rujas	Javier	INO OR006
Maruccia	Elisa	ELE OR20
Marullo	Salvatore	ORG OR111
Marussi	Giovanna	ANA OR065
Marzo	Tiziano	INO OR011
Mascolo	Giuseppe	ABC OR037
Mascolo	Giuseppe	ABC OR038
Masi	Marco	ORG OR044
Massari	Serena	FAR OR036
Massaro	Arianna	TEO OR002
Massaro	Marina	ORG OR054
Mastrangelo	Rosangela	FIS OR074
Mattarozzi	Monica	ANA OR102
Maturi	Mirko	ORG PZ013
Mauriello	Francesco	IND OR059
Mauriello	Francesco	TEC OR002
Mazzapioda	Lucia	ELE OR52
Mazzaracchio	Vincenzo	ANA OR022
Mazzariol	Chiara	INO OR080
Mazzei	Luca	CSB PZ001
Mazzoni	Rita	INO OR043
Mazzucato	Marco	ELE OR12

McLean	John	MAS PL002
Medici	Fabrizio	ORG OR071
Medves	Marco	FIS OR061
Melchior	Andrea	TEC KN004
Melinte	Gheorghe	ANA OR023
Memboeuf	Antony	MAS PL005
Mendolicchio	Marco	TEO OR026
Meninno	Sara	ORG PZ011
Merlo	Francesca	ANA OR110
Mero	Angelica	ORG OR112
Messa	Francesco	ORG OR072
Messina	Grazia	FIS OR007
Messore	Antonella	FAR OR038
Metrangolo	Pierangelo	ORG PZ003
Mezzetta	Andrea	ORG OR062
Mezzomo	Lorenzo	ELE OR63
Micalizzi	Giuseppe	ANA OR111
Miceli	Mariachiara	TEC OR024
Micheletti	Cosimo	IND OR043
Miglio	Vanessa	FIS OR036
Miglione	Antonella	ANA OR046
Migliorati	Valentina	FIS OR121
Migliore	Rossella	ANA OR093
Milanese	Chiara	FIS OR026
Miletto	Ivana	FIS OR062
Milite	Ciro	FAR PZ001
Minella	Marco	ANA OR011
Minero	Claudio	ANA PL001
Minguzzi	Alessandro	ELE KN15
Minnelli	Cristina	ORG OR045
Mocci	Rita	ORG OR066
Moedlinger	Marianne	FIS OR125
Monaci	Linda	MAS KN002
Monciatti	Elisabetta	ORG OR113
Mondello	Luigi	ANA PZ002
Monica	Fabrizio	TEC KN002
Montalbano	Marco	FIS OR114
Montali	Laura	ANA OR125
Montero	Jorge	ELE OR09
Montesarchio	Daniela	ORG PZ006
Montini	Tiziano	IND OR041
Montone	Carmela Maria	ANA OR002
Morandi	Sara	FIS OR077
Moretta	Alma	DID OR006
Morillas Becerril	Lucía	ORG OR046
Moro	Miriam	ELE OR22
Mosconi	Edoardo	INO PZ010
Mostoni	Silvia	INO OR073
Motta	Stefano	TEO OR019
Moyano	Encarnación	MAS PL004
Mulas	Gabriele	FIS OR037

Munzi	Gabriella	TEC OR032
Mura	Monica	FIS OR020
Muraglia	Marilena	FAR OR027
Murgolo	Sapia	ABC OR040
Musazzi	Umberto	TFA OR018
Muscolino	Emanuela	TEC OR047
Musella	Simona	FAR OR005
Musolino	Maria Grazia	IND OR037
Mussini	Patrizia	ANA OR047
Mussini	Patrizia	ELE KN01
Mustorgi	Eleonora	ANA OR133
Musumeci	Francesca	FAR OR003
Nacci	Angelo	ORG OR139
Nale	Angeloclaudio	ELE OR46
Nannuzzi	Chiara	FIS OR112
Nardelli	Francesca	ABC OR012
Nardiello	Donatella	ANA OR012
Narzi	Daniele	TEC OR034
Navacchia	Maria Luisa	ORG OR047
Naviglio	Daniele	ANA OR112
Neese	Frank	INO PZ001
Negri	Fabrizia	TEO KN003
Neri	Giulia	ORG OR055
Nervi	Carlo	INO OR017
Nieto Fabregat	Ferran	ORG OR048
Nomellini	Chiara	FIS OR089
Nori	Valeria	ORG OR065
Notaro	Anna	ORG OR049
Oliva	Eleonora	ANA OR054
Oliveri	Valentina	CSB OR024
Olivieri	Diego	INO OR082
Olivo	Giorgio	ORG OR090
Operamolla	Alessandra	ORG OR056
Orian	Laura	FIS OR100
Orlandi	Manuel	ORG PZ010
Ostacolo	Carmine	FAR OR007
Pagano	Rita	CSB OR020
Pagot	Gioele	ELE OR47
Palazzi	Sergio	DID OR009
Palazzi	Sergio	DID OR014
Palmieri	Sara	ANA OR083
Palmioli	Alessandro	ORG OR050
Panniello	Annamaria	FIS OR050
Panza	Nicola	INO OR013
Paolantoni	Marco	FIS OR116
Paone	Emilia	IND OR038
Papa	Veronica	IND OR069
Pappalardo	Valeria	IND OR055
Pargoletti	Eleonora	ELE OR58
Parmeggiani	Camilla	IND OR030
Parnigotto	Mattia	ELE OR13

Parodi	Adriano	ORG OR030
Parrino	Francesco	TEC OR015
Pascale	Raffaella	MAS OR013
Pasini	Mariacecilia	ORG OR052
Passarini	Fabrizio	ABC KN002
Pastore	Andrea	ANA OR126
Patamia	Vincenzo	ORG OR053
Pavan	Cristina	INO OR003
Pavlos	Nikolaou	ELE OR42
Pavone	Michele	ELE KN64
Pecoraro	Adriana	FIS OR059
Pecoraro	Tania	INO OR034
Peddis	Davide	DID OR007
Peddis	Davide	FIS OR003
Pedone	Alfonso	TEO KN002
Pedrazzani	Riccardo	INO OR046
Pedretti	Silvia	MAS OR002
Pelagatti	Paolo	INO OR053
Pellegrino	Francesco	ANA KN003
Pelosi	Chiara	FIS OR119
Penconi	Marta	FIS OR057
Perathoner	Siglinda	IND KN008
Perego	Carlo	IND KN005
Perinelli	Diego	TFA OR015
Perrella	Fulvio	TEO OR027
Perrone	Daniela	ORG OR051
Peruffo	Nicola	FIS OR046
Petralito	Stefania	TFA OR004
Petri	Elisabetta	ELE OR02
Petrone	Alessio	TEO OR012
Pettazzoni	Luca	ORG OR057
Phan Huu	Andrea	TEO OR032
Piacentini	Emma	TFA OR005
Piacenza	Elena	FIS OR023
Picca	Rosaria Anna	ANA OR066
Picci	Giacomo	INO PZ003
Piccinni	Marco	ELE OR04
Piga	Isabella	MAS OR003
Pigani	Laura	ANA OR048
Pinto	Gabriella	ANA OR013
Pintus	Anna	INO OR044
Pinzi	Luca	FAR OR029
Piovano	Alessandro	FIS OR051
Piovano	Alessandro	IND OR025
Piovesana	Susy	ANA IL001
Pipitone	Giuseppe	IND OR022
Pippione	Agnese	FAR OR001
Pirali	Tracey	FAR KN003
Piras	Federica	ABC OR041
Pirola	Carlo	IND OR068
Pironti	Concetta	ABC OR042

Pirota	Valentina	ORG OR100
Pirro	Fabio	INO PZ006
Pisani	Michela	CSB OR017
Pisani	Silvia	TFA OR021
Pither	Molly	ORG OR092
Platella	Chiara	CSB OR012
Plutino	Maria Rosaria	FIS OR087
Podda	Edoardo	IND OR026
Poggi	Giovanna	FIS OR075
Poli	Federico	ELE OR27
Polo	Annalisa	ELE IL32
Polo	Annalisa	FIS OR032
Ponte	Fortuna	INO PZ004
Porpora	Francesca	ABC OR030
Porto	Michele	FIS OR095
Pota	Giulio	TEC OR013
Potenti	Simone	ORG OR101
Pratesi	Debora	ORG OR093
Prati	Silvia	DID OR013
Pravatto	Pierpaolo	TEO OR033
Prejanò	Mario	INO OR059
Prete	Prisco	IND OR046
Previti	Santo	FAR OR025
Prosa	Mario	FIS OR084
Punta	Carlo	TEC OR003
Punzo	Angela	ANA OR127
Quaglio	Deborah	ORG OR094
Quinto	Maurizio	ANA IL007
Quivelli	Andrea Francesca	ORG OR140
Rabuffetti	Marco	ORG OR141
Radi	Marco	FAR KN004
Ragazzini	Ilaria	ANA OR137
Ragno	Daniele	ORG OR142
Rainer	Alberto	TEC IL001
Ramacciotti	Francesca	ABC OR047
Ranallo	Simona	ANA OR128
Ranaudo	Anna	TEO OR007
Rancan	Marzio	INO OR050
Rapino	Stefania	ELE KN40
Rassu	Giovanna	TFA OR006
Rau	Julietta	FIS KN013
Ravasio	Nicoletta	IND KN001
Ravera	Enrico	INO PZ005
Ravera	Mauro	INO OR029
Rayhane	Zribi	TEC OR037
Reato	Mattia	ELE OR14
Rebeccani	Sara	ELE IL28
Regina	Serena	TEC OR007
Renai	Lapo	ANA OR103
Riccardi	Claudia	CSB OR005
Ricci	Michele	ORG OR102

Ricci	Simona	FIS OR008
Ricciarelli	Damiano	INO OR040
Riela	Serena	ORG OR058
Rigamonti	Luca	INO OR083
Rigon	Carolina	ABC OR031
Rinaldi	Federica	TFA OR007
Ripani	Lorenzo	ELE IL30
Ritacco	Ida	TEO OR005
Riva	Laura	TEC OR006
Rivoira	Luca	ANA OR014
Rizzi	Federica	FIS OR066
Rizzi	Vito	FIS OR039
Rizzo	Carla	ORG OR104
Rizzo	Giorgio	ORG OR143
Rizzuti	Antonino	TEC OR052
Roberto	Grisorio	TEC OR039
Robotti	Elisa	ANA OR040
Rocco	Daniele	ELE OR05
Roda	Barbara	ANA KN012
Rojo	Teofilo	ELE KN73
Roletto	Jacopo	ORG PZ008
Romanelli	Alessandra	CSB OR013
Romanelli	Marco	TFA IL006
Romanucci	Valeria	CSB OR018
Romerio	Alessio	CSB OR014
Rosa-Gastaldo	Daniele	ORG OR091
Rosciardi	Vanessa	FIS OR073
Rossano	Carmelina	IND OR056
Rossetti	Arianna	TEC OR043
Rossetti	Ilenia	IND OR050
Rossi	Christian	INO OR076
Rossi	Federico	FIS OR117
Rossi	Roberto	ORG OR095
Rossin	Andrea	INO OR036
Rossino	Giacomo	FAR OR022
Rosso	Francesca	IND OR062
Rotundo	Laura	ELE IL33
Rovaletti	Anna	TEO OR021
Roverso	Marco	ANA OR084
Ruffino	Roberta	FIS OR012
Ruggieri	Silvia	INO OR010
Russina	Olga	FIS OR123
Russo	Laura	ORG OR096
Russo	Luigi	CSB OR007
Russo	Patrizio	ORG OR144
Russo	Vincenzo	IND OR019
Sabbatini	Luigia	ANA PZ001
Sabbatini	Simona	TEC OR008
Sabuzi	Federica	ORG OR103
Sacchetti	Annalisa	IND OR012
Sacco	Giovanni	ORG OR097

Sacco	Pasquale	FIS OR055
Saielli	Giacomo	TEO OR011
Sainas	Stefano	FAR OR032
Salafia	Fabio	ANA OR032
Salerno	Tania	ANA OR055
Saliu	Francesco	ABC OR018
Salvestrini	Stefano	FIS OR120
Salvino	Rosachiara Antonia	FIS OR045
Salvitti	Chiara	INO OR009
Sanadar	Martina	TEC OR049
Sandri	Giuseppina	TFA OR019
Sangiorgi	Nicola	IND OR042
Sanna Angotzi	Marco	FIS OR091
Sannino	Gennaro	ELE OR38
Sannino	Gennaro	ELE OR38
Sansoni	Simone	FIS OR031
Santalucia	Rosangela	FIS OR104
Santamaria	Monica	ELE KN24
Santi	Cristina Manuela	ORG OR098
Santini	Saul	ANA OR015
Santino	Federica	ORG OR099
Santoro	Antonio	INO OR079
Santulli	Federica	INO OR028
Sarcina	Lucia	ANA OR075
Sardella	Roccaldo	ANA IL008
Sartori	Andrea	ORG OR124
Sartori	Emanuela	FIS OR027
Sassi	Paola	FIS KN002
Satira	Antonella	TEC OR014
Sawssen	Slimani	ABC OR014
Sbrascini	Leonardo	ELE OR70
Scala	Angela	ORG OR125
Scalarone	Dominique	ABC OR051
Scalvini	Laura	FAR OR008
Scattolin	Thomas	INO OR015
Scavetta	Erika	ANA IL002
Schiavo	Eduardo	TEO PZ004
Sciacca	Claudia	ORG OR077
Sciarrone	Danilo	ANA OR056
Sciutto	Giorgia	ANA OR041
Scoditti	Stefano	INO OR026
Scognamiglio	Monica	ORG OR126
Scorciapino	Andrea	FIS KN015
Scroccarello	Annalisa	ANA OR129
Scuderi	Debora	FIS KN006
Serafini	Ilaria	ABC OR013
Serafini	Martina	IND OR033
Sessoli	Roberta	INO PZ009
Severini	Leonardo	FIS OR127
Sfragano	Patrik	ELE OR44
Sgaravatti	Elena	CSB KN004

Sgherza	Damiano	ABC OR053
Sicilia	Emilia	TEO KN001
Siciliano	Giulia	FIS OR109
Silipo	Alba	ORG OR127
Silveri	Filippo	ANA OR024’
Silvestri	Teresa	TFA OR016
Simari	Cataldo	FIS KN014
Simeone	Felice	ABC OR016
Siracusa	Laura	ORG OR128
Slimani	Sawssen	FIS OR005
Sole	Roberto	IND OR007
Sologan	Maria	ORG OR105
Sorbelli	Diego	TEO OR028
Sorbi	Claudia	FAR OR033
Spadavecchia	Serena	ABC OR052
Spanu	Davide	ANA OR094
Speghini	Adolfo	INO OR078
Spinaci	Andrea	FAR OR002
Spinello	Angelo	CSB OR026
Spitaleri	Luca	INO OR012
Sportelli	Maria Chiara	ANA OR122
Spyrakis	Francesca	FAR OR035
Staffolani	Antunes	ELE OR54
Stefania	Rachele	ORG OR129
Stefanucci	Azzurra	FAR OR040
Stener	Mauro	TEO KN004
Stevenazzi	Andrea	FAR KN007
Straniero	Valentina	FAR OR026
Stucchi	Marta	INO OR081
Tabanelli	Tommaso	IND OR003
Tabasso	Silvia	IND OR052
Taddeo	Francesco	IND OR009
Tadini-Buonisegni	Francesco	CSB OR016
Taghavi	Somayeh	IND OR021
Tamborini	Lucia	FAR OR015
Tanini	Damiano	ORG OR078
Tartaglia	Angela	MAS OR012
Tasinato	Nicola	TEO PZ006
Tassone	Giusy	CSB OR015
Tatini	Duccio	FIS OR124
Tavani	Francesco	FIS OR083
Tecilla	Paolo	ORG PZ002
Terraneo	Giancarlo	CSB OR025
Terraneo	Giancarlo	TEC OR030
Terzi	Alberta	FIS OR017
Tesauro	Diego	INO OR065
Tessore	Francesca	INO OR067
Testa	Edoardo	TEC OR048
Testoni	Antonio	DID OR008
Tiboni	Mattia	TFA OR008
Tiecco	Matteo	ORG OR114

Timoncini	Andrea	ABC OR026
Tira	Roberto	CSB OR019
Tocci	Elena	TEO OR014
Tocco	Davide	FIS OR054
Toffanin	Stefano	FIS OR079
Toigo	Christina	ELE OR69
Tomassi	Stefano	FAR OR041
Torrini	Francesca	ANA OR130
Toso	Alessandra	IND OR013
Tosoni	Sergio	TEO OR004
Tranchida	Peter	ANA OR057
Travagliante	Gabriele	CSB OR028
Tribbia	Michele	ELE OR76
Tricase	Angelo	ANA OR049
Trifiletti	Vanira	FIS OR029
Tripaldi	Laura	TEC OR023
Trovato	Emanuela	ANA OR033
Tseberlidis	Giorgio	INO OR038
Tsurumaki	Akiko	ELE OR61
Tubaro	Cristina	INO OR018
Tuccillo	Mariarosaria	FIS OR033
Tuccitto	Nunzio	FIS OR013
Turano	Paola	CSB KN002
Turco	Lucilla	FAR OR030
Turnaturi	Rita	FAR OR010
Turrini	Federica	ANA OR042
Tursi	Antonio	FIS OR042
Uliassi	Elisa	FAR OR034
Vacca	Paolo	IND KN009
Valente Chavez Lozano	Marco	ABC OR049
Valenti	Giovanni	ELE KN10
Valentini	Federica	ORG OR115
Valgimigli	Luca	ORG OR130
Valsecchi	Cecile	ANA OR058
Vanni	Matteo	INO PZ007
Vanti	Giulia	TFA OR020
Vanzan	Mirko	TEO OR003
Varvaro	Gaspare	TEC OR050
Vasa	Kristian	ORG OR107
Velino	Cecilia	ABC OR004
Velino	Cecilia	ABC OR024
Venanzi	Mariano	DID IL001
Venditti	Iole	INO OR064
Venezia	Virginia	TEC OR001
Ventimiglia	Alessia	IND OR054
Vento	Fabiana	IND OR018
Ventura	Giovanni	ANA KN008
Vercelli	Barbara	ELE OR36
Versaci	Daniele	ELE OR71
Vezzù	Keti	ELE OR60
Vincenti	Flaminia	MAS OR015

Vitale	Alessandra	TEC OR051
Vitiello	Rosa	IND OR066
Vitola	Giuseppe	ABC OR044
Vitone	Daniele	CSB OR023
Vivado	Davide	ANA OR016
Vizza	Martina	ANA OR050
Volanti	Mirco	ABC OR039
Vona	Danilo	ORG OR131
Voronov	Aleksandr	IND OR008
Vottero	Eleonora	FIS OR093
Vottero	Eleonora	IND OR004
Weidenkaff	Anke	INO IL002
Wetzl	Cecilia	ELE IL29
Winter	Roland	FIS KN008
Xiufang	He	ELE OR39
Zanardi	Chiara	ANA IL003
Zanchin	Giorgia	ORG OR073
Zani	Lorenzo	ORG OR085
Zanini	Roberta	ABC OR027
Zanut	Alessandra	ELE OR41
Zarrelli	Armando	ABC OR019
Zelenay	Piotr	ELE IL50
Zendri	Elisabetta	ABC OR048
Zennaro	Federtica	ABC OR057
Zianni	Rosalia	MAS OR007
Ziccarelli	Ida	ORG OR146
Zippilli	Claudio	ORG OR079
Zoccali	Mariosimone	ANA PZ003
Zoli	Maddalena	ELE OR25
Zoppi	Giulia	IND OR044
Zucca	Antonio	INO OR071
Zuliani	Alessio	FIS OR041

INDICE COMUNICAZIONI POSTER

Begni	Federico	FIS P0004
Belay	Masho	ANA P0010
Bella	Federico	ELE P0001
Bellomo	Chiara	INO P0009
Bellomo	Chiara	INO P0010
Benedetti	Michele	INO P0011
Benzi	Alice	ORG P0011
Bernardini	Massimo	IND P0003
Berto	Silvia	ANA P0017
Bertuletti	Susanna	ORG P0012
Bertuletti	Susanna	ORG P0111
Bevilacqua	Matteo	INO P0012
Bhela	Irenepreet	FAR P0002
Bianchi	Eleonora	TFA P0004
Bianco	Mariachiara	MAS P013
Bianco	Mariacristina	ANA P0072
Biancolillo	Alessandra	ANA P0031
Bianconi	Elisa	FAR P0022
Bianconi	Tommaso	FIS P0005
Billeci	Floriana	ORG P0013
Bisbal Lopez	Lydia	ORG P0014
Blanco	Ignazio	TEC P0001
Bocchinfuso	Gianfranco	FIS P0006
Bona	Beatrice	FIS P0007
Bonasera	Aurelio	FIS P0008
Bonciarelli	Stefano	ORG P0015
Bortolamiol	Enrica	INO P0013
Boselli	Monica	ORG P0016
Bosi	Adele	ABC P0001
Bozza	Desiree	ANA P0004
Brandiele	Riccardo	ELE P0002
Brigliadori	Andrea	IND P0041
Brouziotis	Antonios Apostolos	ANA P0097
Brucoli	Jacopo	ORG P0017
Brugnetti	Gabriele	ELE P0003
Bruno	Maria Chiara	TFA P0005
Bufano	Mariana	FAR P0003
Bugatti	Kelly	ORG P0018
Buonocore	Michela	FAR P0023
Buratti	Alessandro	ANA P0044
Bussoli	Guido	INO P0014
Cafiero	Claudia Maria	CSB P0006
Calamante	Massimo	ORG P0019
Calì	Federico	FIS P0009
Callone	Emanuela	TEC P0002
Camarero Gonzalez	Patricia	ORG P0020
Cambiotti	Elena	FIS P0010
Camillo Testa	Maria Rita	ANA P0092
Campanella	Beatrice	ANA P0032
Campolucci	Marta	FIS P0011
Cantarini	Mattia	FAR P0004

Cappitti	Alice	IND P0004
Cardellicchio	Francesco	ABC P0002
Cardellicchio	Francesco	ABC P0003
Cardellicchio	Nicola	ABC P0015
Cardiano	Paola	ANA P0062
Carignani	Elisa	FIS P0012
Carnamucio	Federica	ANA P0073
Carraro	Massimo	ORG P0021
Carrozza	Debora	INO P0015
Carta	Paola	FIS P0013
Casadidio	Cristina	TFA P0006
Casale	Monica	ANA P0033
Casiello	Michele	ORG P0022
Casini	Andrea	FIS P0014
Casiraghi	Antonella	FAR P0024
Casiraghi	Antonella	TFA P0036
Castagnotto	Elena	ABC P0036
Castellaneta	Andrea	MAS P001
Castiglioni	Michele	ABC P0029
Catauro	Michelina	TEC P0003
Catenacci	Laura	TFA P0007
Catenacci	Laura	TFA P0008
Catinella	Giorgia	FAR P0025
Catinella	Giorgia	ORG P0023
Cattaneo	Stefano	INO P0016
Cavalleri	Matteo	INO P0017
Cecinato	Angelo	ABC P0023
Cecinato	Angelo	ABC P0025
Cecinato	Angelo	ABC P0026
Cerra	Sara	INO P0018
Cerri	Luca	TFA P0009
Cerveri	Alessandro	ORG P0024
Cescon	Mirco	ANA P0045
Chen	Cheng Giuseppe	FIS P0015
Chiarcos	Riccardo	IND P0005
Chiarello	Matteo	ANA P0078
Chilla	Giuseppe	FIS P0016
Chindamo	Giulia	TFA P0010
Chino	Marco	INO P0019
Chirco	Gabriella	ABC P0004
Ciaffaglione	Valeria	FAR P0005
Ciamaritaro	Veronica	FIS P0017
Cianciusi	Annarita	FAR P0006
Cicchi	Stefano	ORG P0025
Cicco	Luciana	ORG P0026
Ciccola	Alessandro	ABC P0037
Ciccone	Lidia	FAR P0045
Cimino	Cinzia	TFA P0011
Cinelli	Giuseppe	FIS P0018
Cipriano	Alessandra	FAR P0046
Claudia	Claudia	CSB P0005

Clemente	Mariangela	ORG P0027
Cofelice	Martina	FIS P0019
Cogliano	Tommaso	IND P0006
Colaiezzi	Roberta	INO P0020
Compagnucci	Tommaso	ORG P0028
Comparini	Lucrezia Margherita	ORG P0029
Conelli	Daniele	TEC P0004
Coniglio	Davide	MAS P005
Consiglio	Giuseppe	TEC P0005
Consiglio	Giuseppe	TEC P0006
Consumi	Marco	ANA P0005
Conte	Francesco	IND P0007
Conte	Gemma	TFA P0012
Coppola	Carmen	ORG P0030
Coppolino	Carmelo	ANA P0046
Coppolino	Carmelo	ANA P0047
Corazzari	Ingrid	INO P0021
Corradini	Danilo	ANA P0023
Corradini	Danilo	ORG P0031
Corrente	Giuseppina Anna	FIS P0020
Corsini	Maddalena	TFA P0013
Cortesi	Rita	TFA P0014
Costa	Jessica	FIS P0021
Costanzo	Giuliana	FAR P0047
Costi	Maria Paola	FAR P0026
Crescenzi	Maria Assunta	MAS P024
Cressoni	Chiara	INO P0022
Croce	Lucia	ANA P0024
Cucciniello	Raffaele	ABC P0016
Curri	M. Lucia	FIS P0068
Curti	Federica	ORG P0032
D’Amore	Teresa	MAS P014
D’Auria	Maurizio	ORG P0033
De Angelis	Martina	ORG P0034
De Beni	Eleonora	ABC P0009
De Castro	Federica	INO P0023
De Luca	Erik	INO P0024
De Santis	Serena	TEC P0007
De Soricellis	Giulia	INO P0025
De Zotti	Marta	ORG P0035
Decandia	Gianfranco	ORG P0036
Decandia	Modesto	FAR P0048
Decavoli	C.	ORG P0037
Del Regno	Rocco	ORG P0038
Deleo	Alessandro	FAR P0007
Dell’Accantera	Davide	ORG P0039
Della Valle	Maria	CSB P0007
DellaLatta	Elisa	FIS P0022
Denti	Vanna	MAS P010
Di Bello	Elisabetta	FAR P0008
Di Berto Mancini	Marika	ORG P0040

Di Lecce	Roberta	ORG P0041
Di Lorenzo	Flaviana	ORG P0042
Di Matteo	Francesca	FAR P0049
Di Natale	Giuseppe	MAS P007
Di Pietro	Roberto	ANA P0011
Di Sarno	Veronica	FAR P0053
Di Vito Nolfi	Giuseppe	ORG P0043
Diego	Diego	CSB P0002
Dilauro	Giuseppe	ORG P0044
Dolla	Tarekegn	INO P0026
Donadio	Anna	INO P0086
Donato	Paola Agata	ANA P0048
Donato	Simone	IND P0008
Duro	Ida	MAS P023
Fabbri	Debora	ANA P0025
Fabbri	Lorenzo	ANA P0036
Fabbri	Lorenzo	ANA P0037
Fabbri	Roberta	ORG P0112
Facchinetti	Irene	ELE P0004
Faggiano	Antonio	ABC P0033
Fagiolari	Lucia	TEC P0008
Falgiani	Annamaria	ANA P0012
Fallica	Antonino Nicolò	FAR P0059
Fanizzi	P. Francesco	INO P0028
Farinini	Emanuele	ANA P0034
Fasano	V.	ORG P0045
Faverio	C.	ORG P0046
Feoli	Alessandra	FAR P0027
Fermo	Paola	ABC P0005
Ferracane	Antonio	ANA P0049
Ferrara	Chiara	ELE P0005
Ferrauto	Giuseppe	INO P0029
Ferrone	Vincenzo	ANA P0050
Ferrone	Vincenzo	ANA P0051
Fioco	David	INO P0030
Fiore	Luca	ANA P0079
Forghieri	Giulia	IND P0009
Forgione	Rosa	ORG P0047
Forleo	Tiziana	ANA P0018
Formaggio	Fernando	CSB P0008
Formaggio	Fernando	ORG P0048
Fornarini	Simonetta	INO P0031
Forte	Jacopo	TFA P0015
Foschi	Martina	ANA P0035
Fouad Manar	Ahmed	INO P0032
Franca	Marina	INO P0033
Francesca	Francesca	ABC P0038
Franchina	Flavio	ANA P0052
Frassati	Stefano	ANA P0013
Fratoddi	Ilaria	INO P0034
Fresch	Elisa	FIS P0024

Gabano	Elisabetta	INO P0035
Gagliardi	Agnese	TFA P0016
Galletti	Gabriele	IND P0010
Gallucci	Noemi	FIS P0025
Gandini	T.	ORG P0049
Gazzillo	Erica	ORG P0050
Gazzurelli	Cristina	INO P0036
Gentile	Antonio	ELE P0006
Geppi	Marco	FIS P0026
Giacobello	Fausta	FIS P0027
Giacomantonio	Roberto	ORG P0051
Giacomazzo	Gina	INO P0037
Giancaspro	Mariangela	FIS P0028
Giannessi	Giulio	FIS P0029
Giavazzi	Davide	TEO P0001
Gigli	Matteo	INO P0038
Gili	Marilena	MAS P015
Giovanna	Valentino	CSB P0020
Giurlani	Walter	ANA P0038
Gobbo	Alberto	INO P0039
Gottuso	Alessandro	FIS P0030
Gramazio	Pio	IND P0011
Grandinetti	Bruno	IND P0012
Grassiri	Brunella	TFA P0017
Grassiri	Brunella	TFA P0018
Grassiri	Brunella	TFA P0019
Grecchi	Sara	ANA P0039
Grifagni	Deborah	CSB P0009
Grilli	Davide	FIS P0031
Grillo	Giorgio	IND P0013
Grillo	Giorgio	IND P0043
Guaragnone	Teresa	FIS P0032
Guglielmero	Luca	INO P0040
Guidotti	Matteo	IND P0014
Gullo	G.	ORG P0052
Hanieh	Patrizia N.	TFA P0020
Herbrik	F.	ORG P0053
Iammarino	Marco	ANA P0026
Ielo	Ileana	FIS P0033
Imparato	Claudio	TEC P0009
Ioele	Giuseppina	TFA P0037
Iovino	Pasquale	ABC P0017
Iucci	Giovanna	INO P0041
Izzi	Margherita	ANA P0093
Jiritano	Antonio	ORG P0054
Jorea	Alexandra	ORG P0055
Krstic	Milena	ORG P0056
La Gatta	Salvatore	INO P0042
La Parola	Valeria	IND P0015
La Tella	Roberta	ANA P0053
Lagostina	Valeria	INO P0043

Lamanna	Giuseppe	FAR P0052
Landi	Noemi	FIS P0034
Lando	Gabriele	ANA P0074
Landrini	Martina	INO P0044
Lanza	Valeria	CSB P0010
Laudadio	Emiliano	TEC P0010
Lembo	Antonio	ORG P0057
Leonardi	Costanza	ORG P0058
Lettieri	Mariagrazia	ANA P0080
Licen	Sabina	ANA P0081
Lievore	Giulio	ANA P0007
Ligorio	Simona	MAS P009
Lippolis	Martina	ORG P0059
Livolsi	Simone	IND P0016
Lo Vecchio	Carmelo	ELE P0007
Locardi	Federico	FIS P0036
Locatelli	Marcello	ANA P0054
Locatelli	Marcello	ANA P0082
Lombardi	Lorenzo	ORG P0060
Longo	Alessandra	FIS P0037
Longo	Edoardo	ORG P0061
Longo	Lilia	IND P0017
Longobardi	Francesco	ANA P0101
Lopresti	Ludovica	CSB P0011
Loro	Camilla	ORG P0062
Luciani	Lorenzo	INO P0045
Luckham	Stephen	TEC P0011
Lusardi	Matteo	FAR P0009
Macchioni	Alceo	INO P0046
Madabeni	Andrea	FIS P0038
Magnano	Greta	ANA P0098
Maisuradze	Mariam	ANA P0094
Maletti	Laura	ANA P0027
Mandato	Maria	MAS P016
Mandrioli	Roberto	FAR P0028
Manetto	S.	ORG P0063
Manfredi	Marcello	MAS P008
Manghi	Maria Chiara	ABC P0039
Mangini	Anna	TEC P0012
Mangraviti	Domenica	ANA P0028
Manzotti	Mattia	INO P0047
Maramai	S.	ORG P0064
Marassi	Valentina	ANA P0083
Marchesi	Elena	ORG P0065
Marchesi	Massimo	ABC P0022
Marchetti	A.	ORG P0067
Marchetti	Roberta	ORG P0066
Marchettini	Nadia	ABC P0012
Marcì	Giuseppe	TEC P0013
Margani	Fatima	TEC P0014
Mari	Matteo	INO P0048

Marino	Carmen	FAR P0029
Marseglia	Angela	ORG P0068
Martinuzzi	Stefano	ANA P0040
Martinuzzi	Stefano	ANA P0041
Marzano	Simona	CSB P0012
Mascolo	Giuseppe	ABC P0030
Maspero	Marco	FAR P0030
Massardo	Sara	FIS P0039
Maurelli	AnnaMaria	FIS P0040
Mazzariol	Chiara	INO P0049
Mazzilli	Valerio	FIS P0041
Mazzoccanti	G.	ORG P0069
Mazzotta	Elisabetta	ANA P0042
Mazzotta	Sarah	FAR P0010
Mazzucato	Marco	ELE P0009
Mecarelli	Enrica	MAS P006
Melchiorre	Massimo	INO P0050
Meneghetti	Fiorella	FAR P0031
Mentana	Annalisa	MAS P017
Mercadante	Alessandro	ORG P0070
Mercuri	Giorgio	INO P0051
Merlo	Francesca	ANA P0055
Messori	Alessandro	INO P0052
Miele	Dalila	TFA P0021
Migliore	Claudio	IND P0018
Milana	Paola	INO P0053
Milanesi	Francesco	ORG P0071
Milani	Barbara	INO P0054
Milardi	Danilo	CSB P0013
Milone	Marco	ORG P0072
Mingoia	Francesco	FAR P0011
Mizzoni	Silvia	INO P0055
Molteni	Letizia	ORG P0073
Monopoli	Antonio	ORG P0074
Montanari	Serena	FAR P0032
Monti	Marta	TEO P0002
Moreira	Miguel	ORG P0075
Morelli	Carlo F.	ORG P0076
Morena	A.	ORG P0077
Moretti	Elisa	INO P0056
Moretti	Giulia	FIS P0043
Mori	Matteo	FAR P0012
Moriggi	Francesco	TEC P0015
Morina	Riccardo	ELE P0010
Moscone	Danila	ANA P0019
Muccilli	V.	ORG P0078
Musci	Pantaleo	ORG P0079
Mustorgi	Eleonora	ANA P0029
Nacci	Tommaso	ABC P0027
Nagendra	Baku	IND P0019
Napolitano	Ettore	ORG P0080

Nardi	Alessandro Nicola	FIS P0044
Nardiello	Donatella	ANA P0064
Nardiello	Donatella	ANA P0065
Natali	Daniele	IND P0020
Naviglio	Daniele	ANA P0008
Negro	Enrico	ELE P0011
Nicosia	Angelo	IND P0021
Nigro	Maria	ABC P0032
Niknam	Fatemeh	INO P0057
Nocchetti	Morena	INO P0005
Noormohammadi	Eshagh	ELE P0012
Notardonato	Ivan	ANA P0030
Notardonato	Ivan	ANA P0087
Notarstefano	Valentina	INO P0058
Nottoli	Michele	TEO P0003
Oliveri	Valentina	CSB P0014
Olivito	Fabrizio	ORG P0081
Omelyanchik	Alexander	FAR P0033
Omelyanchik	Alexander	FIS P0045
Ottolini	Michela	FIS P0046
Oulad El Majdoub	Yassine	ANA P0006
Pagano	Flavia	ANA P0099
Pagano	Rosanna	FIS P0047
Pagliaricci	Noemi	INO P0059
Pagliero	Marcello	IND P0022
Pajer	Nicolò	INO P0060
Palagi	Lorenzo	CSB P0015
Palermo	Carmen	ANA P0066
Palucci	Benedetta	ORG P0082
Pampararo	Giovanni	INO P0061
Panunzi	Paola Anna	ELE P0013
Paoletti	Fabiola	MAS P018
Papa	Ester	ABC P0035
Paparo	Rosanna	ANA P0088
Papucci	Costanza	ORG P0083
Parise	Angela	INO P0062
Passarini	Fabrizio	ABC P0040
Pavan	Cristina	INO P0063
Pavletić	Pegi	FAR P0050
Pavoni	Elena	ANA P0014
Peddis	Davide	FIS P0048
Pellis	Giulia	ABC P0006
Pepe	Angela	MAS P020
Pepe	Giacomo	FAR P0034
Perego	Jacopo	IND P0023
Perra	Matteo	TFA P0022
Peruffo	Nicola	FIS P0049
Petrilli	Marzia	ORG P0084
Pianta	Nicolò	ELE P0014
Pierini	Adriano	TEO P0004
Pierri	Martina	ORG P0085

Pietracci	Lorenzo	INO P0064
Pietrobon	Luca	IND P0024
Pietrobon	Luca	IND P0025
Pigliacelli	Claudia	TEC P0016
Pilato	Serena	ORG P0086
Pinna	Marco	ANA P0015
Pinzi	Luca	FAR P0054
Pirodda	Gabriele	TEC P0017
Pirola	Carlo	IND P0026
Pisano	Luisa	ORG P0087
Pittalà	Valeria	FAR P0055
Pizzolato	Marco	IND P0027
Poerio	Teresa	TEC P0018
Pogni	Rebecca	FIS P0051
Porcelli	Francesco	TEC P0019
Porpora	Francesca	ABC P0007
Porporato	Silvia	ELE P0017
Prestia	Tommaso	ORG P0088
Preti	Lorenzo	ORG P0089
Prioglio	Gea	TEC P0020
Priola	Emanuele	INO P0065
Pro	Chiara	INO P0066
Protti	Michele	FAR P0035
Prozzi	Marco	ANA P0016
Puxeddu	Michela	FAR P0056
Quaglia	Giulia	FIS P0052
Quinto	Maurizio	ANA P0056
Quinto	Maurizio	ANA P0089
Racaniello	Giuseppe F.	TFA P0023
Ragone	Rosa	TEC P0021
Rama	Francesco	TFA P0034
Rando	Giulia	FIS P0053
Rando	Maria	INO P0067
Rapacciuolo	Pasquale	ORG P0090
Rapino	Alessandra	TFA P0035
Raspolli Galletti	Maria Anna	IND P0028
Rebeccani	Sara	ELE P0015
Renno	Giacomo	IND P0029
Renzi	Emilia	INO P0068
Riboni	Nicolò	ANA P0067
Ricci	Paola	INO P0085
Ricciardi	Beatrice	TEC P0022
Ricciardi	Maria	ABC P0034
Rigante	Elena	ANA P0063
Rigoletto	Monica	ABC P0041
Ripani	Lorenzo	ELE P0016
Rispoli	Francesco	ORG P0091
Rivoira	Luca	ABC P0018
Rizzardi	Ilaria	IND P0030
Rizzi	Rosanna	FAR P0057
Rizzo	Marco	FAR P0013

Rizzo	S.	TFA P0033
Rizzo	Serena	MAS P019
Roda	Barbara	ANA P0020
Romanelli	Alessandra	CSB P0016
Romani	Daphne	INO P0069
Romano	Giammarco Maria	INO P0070
Romanucci	Valeria	ORG P0092
Rombolà	Alessandro G.	ANA P0057
Romeo	Alessia	TFA P0024
Romeo	Isabella	FAR P0014
Rosa	Roberto	TEC P0023
Rosati	Marta	ORG P0093
Rosetti	Alessia	FAR P0036
Rossi	Ruggero	IND P0031
Ruggeri	Marco	TFA P0025
Russo	Camilla	FAR P0058
Russo	Francesca	ABC P0013
Russo	Simona	INO P0071
Russo	Stefano	TEO P0005
Sabatino	Leonardo	ANA P0090
Saiano	Filippo	ANA P0058
Saladino	Marialuisa	FIS P0054
Salafia	Fabio	ANA P0091
Salamone	Tommaso	INO P0072
Salerno	Alessandra	FAR P0051
Salha	Mohammed	INO P0073
Saliu	Francesco	ABC P0010
Saliu	Francesco	ABC P0011
Saliu	Francesco	MAS P022
Salvador	María	TFA P0026
Salvini	Antonella	IND P0032
Samorì	Chiara	ORG P0094
Sandri	Francesco	IND P0033
Sandri	Francesco	IND P0042
Santarsiere	Alessandro	ORG P0095
Santonoceta	Giuseppina	ANA P0075
Santoro	Angelo	FAR P0037
Sanz	Ines	FAR P0038
Sarti	Elena	ABC P0031
Sartirana	Marta	IND P0034
Satta	Giuseppe	ORG P0096
Saviano	Michele	CSB P0017
Scala	Maria Carmina	FAR P0039
Scandurra	Cecilia	ANA P0084
Scarperi	Andrea	FIS P0055
Schifano	Fabio	INO P0074
Schlich	Michele	TFA P0027
Sciacca	Michele	CSB P0018
Scibetta	Lorenzo	ABC P0024
Scognamiglio	Antonia	FAR P0015
Sebastiani	Jessica	FAR P0060

Secci	Fausto	FIS P0056
Semeraro	Paola	FIS P0057
Severini	Leonardo	FIS P0058
Sfameni	Silvia	FIS P0059
Sgarbossa	Paolo	TEC P0024
Sica	Alfredo	FAR P0040
Sica	Filomena	FIS P0060
Silla	Alessia	ANA P0085
Silvestri	Brigida	TEC P0025
Sirignano	Marco	INO P0075
Smaldone	Gerardina	FAR P0016
Smith	Andrew	MAS P002
Sommonte	Federica	TFA P0028
Sonzini	Paolo	INO P0076
Sorato	Andrea	ORG P0097
Sori	Lorenzo	TEC P0026
Spada	Lucia	ABC P0019
Sparaco	Rosa	FAR P0017
Spatola	Emanuele	ORG P0098
Speciale	Immacolata	ORG P0099
Speltini	Andrea	ANA P0068
Speltini	Andrea	ANA P0086
Sportelli	Maria Chiara	ANA P0095
Squadrone	S.	INO P0027
Stabile	Rita	FAR P0018
Staccioli	Maria Paola	FIS P0067
Stevanin	Claudia	ANA P0059
Stoccoro	Sergio	INO P0077
Tali Shandiz	Shiva	FAR P0019
Taliani	Sabrina	FAR P0061
Tallarida	A. Matteo	ORG P0100
Tammaro	Olimpia	IND P0035
Tarsitano	Martine	TFA P0029
Tartaglia	Angela	MAS P003
Tartaglia	Angela	MAS P004
Tassone	Giusy	CSB P0019
Tesser	Riccardo	IND P0036
Ticali	Pierfrancesco	FIS P0061
Tieuli	Sebastiano	IND P0037
Toma	Lorenzo	ANA P0100
Tomassetti	Mauro	ANA P0021
Tombesi	Alessia	INO P0078
Torta	Gianluca	ABC P0020
Toscanesi	Maria	IND P0038
Tresin	Federica	INO P0079
Tricomi	Jacopo	ORG P0101
Tricomi	Jacopo	ORG P0102
Trilli	Jordan	FAR P0041
Troiani	Anna	MAS P021
Troiani	Anna	TEC P0027
Troiano	Cassandra	FIS P0062

Troiano	Rubina	INO P0080
Truzzi	Cristina	ANA P0060
Tudino	Valeria	FAR P0020
Turco	Rosa	IND P0039
Turrini	Federica	ANA P0069
Vagnoni	Flavio	ANA P0061
Valentini	Francesca	ORG P0103
Valentino	Caterina	TFA P0030
Vanacore	Adele	ORG P0104
Varsalona	Maria	FIS P0063
Venanzi	Mariano	FIS P0064
Vento	Federica	ANA P0070
Verdicchio	Federico	INO P0081
Veronese	Eleonora	ORG P0105
Versaci	Daniele	ELE P0018
Vezzoni	Carlo Alberto	ORG P0106
Vicente-Garcia	Cesar	ORG P0107
Vida	Veronica	ORG P0108
Vigani	Barbara	TFA P0031
Villa	Stefania	FAR P0062
Viteritti	Eduardo	ANA P0071
Vivenzio	Giovanni	FAR P0021
Viviano	Monica	FAR P0063
Vizza	Martina	ANA P0043
Voccia	Maria	IND P0040
Voci	Silvia	TFA P0032
Volanti	Mirco	ABC P0014
Vomeri	Alessandro	INO P0082
Wafa	Aidli	ELE P0019
Xhafa	Sonila	INO P0083
Yousif	Dawod	ORG P0109
Zamperlin	Nico	TEC P0028
Zampieri	Daniele	FAR P0044
Zani	Veronica	FIS P0066
Zecca	Marco	ORG P0110
Zuccaccia	Daniele	INO P0084

SCI2021

14–23 SETTEMBRE 2021

XXVII CONGRESSO NAZIONALE DELLA
SOCIETÀ CHIMICA ITALIANA

ISBN 978-88-94952-24-7
9 788894 952247