Atti del
XXX Congresso della Divisione di Chimica Analitica della Società Chimica Italiana

1973-2023 – I primi 50 anni della Divisione di Chimica Analitica

Palazzo D’Avalos, Città del Vasto (CH)

17-21 Settembre, 2023

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ISBN: 978-88-94952-38-4
© Società Chimica Italiana 2023
Pubblicato online il 17 Settembre 2023
Vasto, Italia
ISBN 978-88-94952-38-4
9 788894 952384

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Comitati

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- Paolo Oliveri (UNIGE)
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Il convegno è organizzato in collaborazione sinergica dei gruppi di ricerca in chimica analitica delle

UNIVERSITÀ DEGLI STUDI DELL'AQUILA
UNITE UNIVERSITÀ DEGLI STUDI DI TERAMO
UNIVERSITÀ DEGLI STUDI DEL MOLISE
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Presentazione

Il Congresso, che la Divisione di Chimica Analitica della Società Chimica Italiana organizza annualmente, vuole essere un punto di incontro e di confronto per tutti coloro che svolgono la propria attività nella ricerca chimico analitica, in modo particolare nella XXX edizione che coincide con i 50 anni dalla costituzione della Divisione di Chimica Analitica (1973 -2023).
Durante il convegno vengono trattati diversi aspetti della chimica analitica, dai settori tradizionali, a quelli più innovativi. In particolare, sono presenti contributi relativi allo sviluppo di teorie, materiali, metodologie e tecniche strumentali per la determinazione composizionale qualitativa e quantitativa di sistemi chimici, progettazione e sviluppo di (bio)sensori, tecniche separative avanzate, sistemi analitici integrati, tecniche e metodi di caratterizzazione, di speciazione e metrologici, anche per misure in campo e/o remote, per l'ambiente, gli alimenti e la diagnostica medica, lo sviluppo ed applicazione di modelli teorici e strumenti chemiometrici per la valutazione di qualità e significatività dell'informazione chimica.

I partecipanti vengono cordialmente invitati a presentare i risultati della propria attività di ricerca in forma di relazioni ad invito, keynotes, relazioni orali che vengono selezionate dal Comitato Scientifico (Direttivo della Divisione).

I principali argomenti di discussione previsti sono i seguenti:

- Alimenti e Nutraceutici
- Ambiente e Beni Culturali
- Bioanalitica e Omics
- Chemiometria e Qualità del Dato
- Chimica Analitica Forense
- Elettroanalitica
- Equilibri in Soluzione e Speciazione
- Green Chemistry
- Sensori e Biosensori
- Spettrometria di Massa
- Spettroscopia Analitica
- Scienza delle Separazioni
- Tossicologia e Salute Umana

Programma dettagliato

DOMENICA-SUNDAY 17/09/2023

17.00-21.00 - Registrazione dei partecipanti

19.00 – 21.00 - Cocktail di benvenuto presso il Giardino Napoletano

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LUNEDI'-MONDAY 18/09/2023

8.30 – REGISTRAZIONE/ REGISTRATION

APERTURA DEL CONGRESSO

SALA / Room: PINACOTECA

L'apertura del congresso, la consegna del Premio Giovane Ricercatore, e tutte le sessioni plenarie che avverranno nella sala Pinacoteca e trasmesse live nella Sala Archeologia e Sala della Cornice. / The opening ceremony, the presentation of the Young Researcher Prize, and **all the plenary sessions** will take place in the Pinacoteca and broadcast in the Archeologia and Cornice rooms.

09.00 – 09.30 - APERTURA DEL CONGRESSO / Opening Ceremony

09.30 – 10.15- **PL1 - Homola Jiří (Institute of Photonics & Electronics, Czech Academy of Sciences)**.

ADVANCES IN PLASMONIC AFFINITY BIOSENSORS FOR MEDICINE

10.15 – 10.35 - Conferenza Vincitore del Premio Giovane Ricercatore.
Dr. Alessandra Biancolillo (Università degli Studi di L'Aquila)

CHEMOMETRICS: THE KEY TO UNRAVEL COMPLEX ANALYTICAL CHEMISTRY DATA

10.40 – 11.10-COFFEE BREAK (Giardino Napoletano)

PL: Plenary
KN: Keynote
O: Oral Contribution

Sessione Parallela: Sensori-Biosensori (SB)-1

SALA / Room: PINACOTECA

Moderatori: Prof.ssa Fabiana Arduini; Prof.ssa Luisa Torsi

11.10 – 11.30 - **KN1-SB** - *COLORIMETRIC LABELS IN LATERAL FLOW IMMUNOASSAYS: CAN WE OVERCOME THE USE OF NOBLE METAL NANOPARTICLES?*

F. Di Nardo, S. Cavalera, L. Anfossi, C. Baggiani
Università degli Studi di Torino

11.30 – 11.45 - **O1-SB** - *DECORATED DNA-BASED SCAFFOLDS AS LATERAL FLOW BIOSENSORS*

S. Brannetti, S. Gentile, A. Chamorro-Garcia, L. Barbero, E. Del Grosso and F. Ricci
Università degli Studi di Roma Tor Vergata

11.45 – 12.00 - **O2-SB** - *ALL-IN-ONE PAPER-BASED MICROFLUIDIC DEVICE FOR PARACETAMOL ELECTROANALYSIS IN ENVIRONMENTAL MATRICES*

A. Miglione, A. Raucci, F. Cristiano, S. Cinti
Università Federico II di Napoli

12.00 – 12.15 – **O3-SB** - *A PAPER-BASED ELECTROCHEMICAL APTASENSOR FOR USER-FRIENDLY THROMBIN DETECTION IN BIOLOGICAL MATRICES*

A. Raucci, G. Sorrentino, A. Miglione, M. Terracciano, G. Oliviero, G. Piccialli, N. Borbone, S. Cinti
Università Federico II di Napoli

12.15 – 12.30 – **O4-SB** - *3D PAPER-BASED ELECTROANALYTICAL DEVICE FOR ALL-IN-ONE CARBARYL ANALYSIS*

S. Fiori, F. Della Pelle, A. Scroccarello, M. Del Carlo, D. Compagnone
Università degli Studi di Teramo

12.30 – 12.45 – **O5-SB** - *BUTTERFLY-LIKE PAPER-BASED MICROFLUIDC POTENTIOMETRIC WEARABLE SENSOR FOR DEHYDRATION MONITORING DURING PHYSICAL ACTIVITY*

L. Fiore, V. Mazzaracchio, A. Antinucci, R. Ferrara, T. Sciarra, F. Lista, F. Arduini
Università degli Studi di Roma Tor Vergata

12.45 – 13.00 – **O6-SB** – *SUSTAINABLE EXTRACTION AND ANALYSIS OF ZINC IN SOIL BY COMBINING A 3D-PRINTED ANALYTICAL TOOL AND PAPER-BASED SCREEN-PRINTED SENSORS*

N. Colozza, D. Aquilani, A. Pizziconi, F. Arduini
Università degli Studi di Roma Tor Vergata

Sessione Parallela: Scienza-Separazioni (SP)-1

SALA / Room: ARCHEOLOGIA

Moderatori: Prof. Danilo Sciarrone; Prof. Aldo Laganà

11.10 – 11.30 - **KN1-SP** - *VIEWS ON THE USES OF COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY-MASS SPECTROMETRY IN FOOD ANALYSIS*

P.Q. Tranchida, M. Zoccali, A. Arena, M. Galletta, A. Ferracane, L. Mondello
Università degli Studi di Messina

11.30 – 11.45 - **O1-SP** - *CRYOGENIC MODULATION GC×GC-QqQMS FOR PESTICIDES DETERMINATION IN HEMP SEED OIL*

A. Arena, M. Zoccali, A. Ferracane, M. Obkircher, H. Sprecher, P.Q. Tranchida, L. Mondello
Università degli studi di Messina

11.45 – 12.00 - **O2-SP** - *UNTARGETED PROFILING AND TARGETED DETERMINATION OF CHIRAL LACTONES IN MARSALA WINES USING HEADSPACE SPME FLOW-MODULATED COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY (ENANTIO×POLAR) WITH TIME-OF-FLIGHT MASS SPECTROMETRY*

M. Galletta, M. Zoccali, P.Q. Tranchida, L. Mondello
Università degli Studi di Messina

12.00 – 12.15 – **O3-SP** - *VACUUM-ASSISTED HEADSPACE-SOLID PHASE MICROEXTRACTION FOR SHORT AND LONG CHAIN FATTY ACIDS IN BIOLOGICAL SAMPLES*

E. Porru, N. Interino, R. Comito, F.S. Violante, J. Fiori
Università degli Studi di Bologna

12.15 – 12.30 – **O4-SP** - *A POWERFUL AF4-MULTIDETECTION METHOD FOR CHARACTERIZATION, QUALITY CONTROL AND PURIFICATION OF SELF-ASSEMBLING PROTEINS FROM ENGINEERED E. coli LYSATES*

S. Giordani, T. Rossi, B. Roda, A. Zattoni, P. Reschiglian, A. Danielli, V. Marassi
Università degli Studi di Bologna

12.30 – 12.45 – **O5-SP** - *QUANTIFICATION OF HEALTH CLAIM-RELEVANT TYROSOL AND 3-HYDROXYTYROSOL IN EXTRA VIRGIN OLIVE OIL AFTER DIRECT HYDROLYSIS*

D. Corradini
CNR Istituto per i Sistemi Biologici

12.45 – 13.00 – **O6-SP** – *POTENTIALITY OF A MIXED-MODE STATIONARY PHASE TO ADDRESS CHALLENGING PEPTIDE PURIFICATION THROUGH PREP-LC*

C. De Luca, G. Lievore, S. Felletti, M. Catani, D. Bozza, M. Macis, A. Ricci, W. Cabri, A. Cavazzini
Università degli Studi di Ferrara

Sessione Parallela: Bioanalitica-omics (B)-1

SALA / Room: SALA DELLA CORNICE

Moderatori: Prof. Aldo Roda; Prof.ssa Maria Careri

11.10 – 11.30 - **KN1-B** - *COMPREHENSIVE GCxGC HIGH RESOLUTION MS AND SELECTIVE ISOLATION OF CHEMICALS IN THE INVESTIGATION OF HUMAN CHEMOSIGNALS ELICITED FROM EMOTIONAL STIMULATION*

T. Bruderer, M. Ripszam, F. Vivaldi, A. Greco, A. Gargano, N. Gomes, A. L. Callara, D. Biagini, S. Ghimenti, T. Lomonaco, G. Semin, E. P. Scilingo, F. Di Francesco
Università degli Studi di Pisa

11.30 – 11.45 - **O1-B** - *FPSE-HPLC-PDA ANALYSIS OF ANTIDEPRESSANTS IN BIOLOGICAL MATRICES*

M. Locatelli, C. D’Ovidio, A.M. Catena, F. Savini, U. de Grazia, A. Kabir, L. Ciriolo, M. Perrucci
Università degli G. d'Annunzio Chieti-Pescara

11.45 – 12.00 - **O2-B** - *RESHAPING OF THE MITOCHONDRIAL PHOSPHOLIPIDOME UPON REMOVAL OF FUSION PROTEINS: AN INVESTIGATION BY HILIC-ESI-FTMS*

A. Castellaneta, I. Losito, V. Porcelli, S. Barile, A. Maresca, V. Del Dotto, V. Losacco, L.S. Guadalupi, C.D. Calvano, V. Carelli, L. Palmieri, T.R.I. Cataldi
Università degli Studi di Bari

12.00 – 12.15 – **O3-B** – *SUPER SILAC-BASED EPIPROTEOMIC AND LABEL-FREE QUANTITATIVE SWATH-MS ANALYSIS OF PANCREATIC CANCER STEM CELLS*

G.Siragusa, J.Brandi, E.Dalla Pozza, R.Noberini, T.Bonaldi, M.Manfredi, E.Marengo, I.Dando, D.Cecconi
Università degli Studi di Verona

12.15 – 12.30 – **O4-B** - *BREATH AND DRIED BLOOD SPOT ANALYSIS COMBINED WITH CARDIOPULMONARY EXERCISE TESTING AND ECHOCARDIOGRAPHY FOR MONITORING HEART FAILURE*

T. Lomonaco, N. R. Pugliese, S. Farnocchia, G. Bertazzo, F. De Angelis, S. Ghimenti, A. Lenzi, D. Biagini, S. Armenia, S. Taddei, S. Masi, F. Di Francesco
Università degli Studi di Pisa

12.30 – 12.45 – **O5-B** - *INVESTIGATION OF ACYLCARNITINE BIOMARKERS IN PROSTATE CANCER TISSUE BY HIGH-RESOLUTION MASS-SPECTROMETRY AND RETENTION TIME PREDICTION*

A. Cerrato, A. Biancolillo, A. Laganà, A. Sciarra, E. Taglioni, A. L. Capriotti
Università degli Studi di Roma Sapienza

12.45 – 13.00 – **O6-B** – *ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY FOR SENSITIVE DETECTION OF FOOD ALLERGENS IN COMPLEX, PROCESSED AND NOVEL FOODSTUFFS*

C.D. Calvano, M. Bianco, G. Ventura, I. Losito, T.R.I. Cataldi
Università degli Studi di Bari Aldo Moro

13.00 – 14.00 - Lunch (libero)

14.00 – 15.00 – Sessione poster / Poster Session: Bioanalitica-Omics (P1-6); Forense, Tossicologia e Salute (P1-10); Scienza delle Separazioni (P1-17); Sensori e Biosensori-1 (P1-12); Elettroanalitica (P1-7).

Sessione Parallela: Sensori-Biosensori (SB)-2

SALA / Room: PINACOTECA

Moderatori: Prof. Francesco Ricci; Prof.ssa Chiara Zanardi

15.00 – 15.20 – **KN2-SB** – *MOLECULAR IMPRINTING AND SENSING TECHNOLOGY: A HAPPY MARRIAGE BASED ON ESTABLISHED AND INNOVATIVE STRATEGIES*

E. Mazzotta, T. Di Giulio, C. Malitesta
Università del Salento

15.20 – 15.35 – **O7-SB** – *MOLECULARLY IMPRINTED NANOGELS IN OPTICAL SENSING*

A.M. Bossi
Università degli Studi di Verona

15.35 – 15.50 – **O8-SB** - *BIO-INSPIRED POLYMERS FROM ENDOGENOUS NEUROTRANSMITTERS: TOWARDS UNIVERSAL PROTEIN IMPRINTING?*

S. Scarano, F. Battaglia, F. Torrini, G. Ciacci, A. Barucci P. Palladino, M. Minunni
Università deli Studi di Firenze

15.50 – 16.05 – **O9-SB** – *ECO-FRIENDLY PREPARED MOLECULARLY IMPRINTED POLYMERIC NANOPARTICLES IN SENSOR DESIGN FOR THE ELECTROCHEMICAL DETERMINATION OF AMOXICILLIN*

S. Di Masi, C. Malitesta
Università degli Studi del Salento

16.05 – 16.20 – **O10-SB** – *A GUANOSINE-DERIVED SUPRAMOLECULAR HYDROGEL WITH PEROXIDASE-LIKE ACTIVITY AS A NEW TOOL FOR HYDROGEN PEROXIDE DETECTION*

D. Calabria, S. Pieraccini, E. Lazzarini, A. Pace, I. Trozzi, M. Guardigli, S. Masiero, M. Mirasoli
Università degli Studi di Bologna

16.20 – 16.35 – **O11-SB** – *A VERSATILE APPROACH FOR ACHIEVING METAL ION MEDIATED INTERACTIONS ON POROUS SILICON INTERFEROMETERS*

T. Di Giulio, F. Gagliani, C. Malitesta, M. Corsi, G. Barillaro, E. Mazzotta
Università degli Studi del Salento

16.35 – 17.00-COFFEE BREAK (Giardino Napoletano)

17.00 – 17.15 – **O12-SB** – *A NANO-PLASMONIC BIOSENSOR FOR FAST AND HIGHLY SENSITIVE DETECTION OF NANOPLASTICS*

M. Seggio, F. Arcadio, L. Zeni, N. Cennamo, A. M. Bossi
Università degli Studi di Verona

17.15 – 17.30 – **O13-SB** – *COMBINING NEW LUCIFERASE MUTANTS WITH METAL-ORGANIC-FRAMEWORKS TO DEVELOP NEW BIOSENSING TOOLS*

D. Gregucci, M.M. Calabretta, E. Michelini
Università degli Studi di Bologna

17.30 – 17.45 – **O14-SB** – *A DISPOSABLE IMMUNOSENSOR FOR DETECTION OF SALIVARY MMP-8 AS BIOMARKER OF PERIODONTITIS*

C. Tortolini, V. Gigli, A. Angeloni, T. K.T. Nguyen, R. Antiochia
Università degli Studi di Roma Sapienza

17.45 – 18.00 – **O15-SB** – *DIRECT DETECTION OF SINGLE POINT MUTATION BY SUPERPARAMAGNETIC PARTICLES-ENHANCED SPR BIOSENSOR IN LIQUID BIOPSY*

N. Bellassai, R. D'Agata, G. Spoto
Università degli Studi di Catania

Sessione Parallela: Forense, Tossicologia-Salute (FT)

SALA / Room: ARCHEOLOGIA

Moderatori: Prof. Manuel Sergi; Prof. Marco Vincenti

15.00 – 15.20 – **KN1-FT** – *ADVANCED ANALYTICAL STRATEGIES FOR DETECTION OF FORENSIC RELEVANT COMPOUNDS*

A. Lombardozzi, S. Napoletano, M. D'Elia, G. Di Francesco, F. Ciocchetti, M. Croce, F. Vincenti, C. Montesano, M. Sergi, F. Marini, R. Curini
Ministry of Interior – Department for Public Security Central Anticrime Directorate of the Italian State Police– Forensic Science Police Service (DAC-SPS), Rome

15.20 – 15.35 – **O1- FT** – *MULTIVARIATE MODELLING IN HAIR TESTING – MODELLING THE HAIR COLOR BIAS AGAINST DISCRIMINATION*

M. Vincenti, M. Piras, N. Castellino, A. Salomone, E. Alladio
Università degli Studi di Torino

15.35 – 15.50 – **O2- FT** – *METHOD FOR DIRECT ENANTIOMER DETERMINATION OF METHORPHAN IN SEIZED DRUGS AND BIOLOGICAL SPECIMENS BY MEANS OF CHIRAL HPLC-MS/MS*

C. Coppolino, T. M. G. Salerno, G. Frison, L. Zamengo, P. Donato, L. Mondello
Università degli Studi di Messina

15.50 – 16.05 – **O3- FT** – *STUDY OF METABOLOMIC PROFILE ALTERATIONS INDUCED BY OPIOIDS IN MURINE MODELS BY UHPLC-HRMS*

G. Di Francesco, M. Croce, F. Vincenti, C. Montesano, M. Marti, M. Sergi, R, Curini
Università degli Studi di Roma Sapienza

16.05 – 16.20 – **O4- FT** – *DEVELOPMENT OF A NEW LIQUID PHASE MICROEXTRACTION METHOD FOR THE DETERMINATION OF SEVERAL ILLICIT DRUGS AND NPS IN ORAL FLUID BY HPLC-MS/MS ANALYSIS*

M. Croce, G. Di Francesco, F.Marini, F. Vincenti, C. Montesano, M. Sergi, R. Curini
Università degli Studi di Roma Sapienza

16.20 – 16.35 – **O5- FT** – *COMPARATIVE SPECTROSCOPY STUDIES OF KNOWN VERSUS NEW SYNTHETIC CANNABINOID FAMILIES*

V. Greco, A. B. Carbonaro, V. Buccilli, P. Maida and A. Giuffrida
Università degli Studi di Catania

16.35 – 17.00-COFFEE BREAK (Giardino Napoletano)

17.00 – 17.15 – **O6- FT** – *ORIGAMI PAPER-BASED DEVICE AS AN INEXPENSIVE TOOL FOR IDENTIFYING URINE ADULTERATION IN A FORENSIC TOXICOLOGY CONTEXT*

G. Musile, Y. Agard, S. Pesavento, F. Bortolotti, F. Tagliaro
Università degli Studi di Verona

17.15 – 17.30 – **O7- FT** – *VIRGIN AND PHOTODEGRADED MICROPLASTICS IMPACT THE INFLAMMATORY RESPONSE OF VASCULAR MUSCLE CELLS*

T. Lomonaco, E. Persiani, I. Gisone, E. Ceccherini, A. Cecchettini A. Corti, D. Biagini, S. Ghimenti, F. Di Francesco, V. Castelvetro, F. Vozzi
Università di Pisa

17.30 – 17.45 – **O8- FT** – *HEPATIC CONCENTRATIONS OF RARE EARTH ELEMENTS IN DOMESTIC DOGS AND APENNINE WOLVES FROM CENTRAL ITALY*

M. Bellocci, S.V.P Defourny, C. Merola, R. Salini, V. Melai, G. Romeo, L. Lomellini, A. Coccaro, G. Scortichini, A. Petrini
Università degli Studi di Teramo; Istituto Zooprofilattico Sperimentale dell'Abruzzo e Molise "G. Caporale"

17.45 – 18.00 – **O9- FT** – *THE ITALIAN TECHNICAL SPECIFICATION UNI/TS 11868:2022 FOR THE DETERMINATION OF SULPHITES IN MEAT*

M. Iammarino, G. Berardi, A. Di Taranto
Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata

18.00 – 18.15 – **O10- FT** – *THE POTENTIAL OF THE STABLE ISOTOPE RATIO ANALYSIS TO ENSURE THE AUTHENTICITY OF FOOD SUPPLEMENTS*

M. Perini, S. Pianezze
Fondazione Edmund Mach

Sessione Parallela: Bioanalitica-omics-2

SALA / Room: SALA DELLA CORNICE

Moderatori: Prof.ssa Laura Anfossi; Prof.ssa Sandra Furlanetto

15.00 – 15.20 – **KN2-B** – *SIMILAR BUT NOT IDENTICAL: THE HUNT FOR BINDING COOPERATIVITY IN ARTIFICIAL ANTIBODIES*

L. Anfossi, C. Baggiani, S. Cavalera, F. Di Nardo
Università degli Studi di Torino

15.20 – 15.35 – **O7-B** – *ELUCIDATION OF ZWITTERIONIC AND POSITIVELY CHARGED METABOLITES IN PROSTATE CANCER BY DEDICATED UNTARGETED METABOLOMICS*

A. Cerrato, A. Laganà, S. Piovesana, R. Tauler, A.L. Capriotti
Università degli Studi di Roma Sapienza

15.35 – 15.50 – **O8-B** - *THERMAL STAMPING OF LASER-REDUCED GRAPHENE OXIDE FOR DIRECT ELECTRON TRANSFER-TYPE BIOSENSORS*

D. Paolini, F. Della Pelle, F. Silveri, P. Bollella, A. Scroccarello, L. Torsi, D. Compagnone
Università degli Studi di Teramo

15.50 – 16.05 – **O9-B** – *MONITORING OF THE IMMUNE RESPONSE TO SARS-COV-2 AFTER VACCINATION AND RECOVERY BY LATERAL FLOW IMMUNOASSAY*

S. Cavalera, B. Colitti, C. Nogarol, C. Guiotto, D. Cosseddu, T. Serra, V. Testa, F. Di Nardo, C. Baggiani, S. Rosati, L. Anfossi
Università degli Studi di Torino

16.05 – 16.20 – **O10-B** – *A MULTI-OMICS INVESTIGATION ON BIOLUMINESCENCE IN DEEP SEA FISHES*

N. Interino, E. Esposito, C. Corinaldesi, A. Fumanti, E. Buschi, M. Tangherlini, E. Rastelli, A. Sagrati, G. Palladino, A. Dell'Anno, S. Rampelli, D. Scicchitano, P. Battaglia, R. Danovaro, M. Candela, J. Fiori
Università degli Studi di Bologna

16.20 – 16.35 – **O11-B** – *DESIGN OF EXPERIMENT AND UNTARGETED ANALYSIS: AN APPLICATION TO MONITORING EMERGING CONTAMINANTS IN CLAIMS*

M. Roverso, S. Boscolo, T. Paravano, S. Pettenuzzo, P. Centomo, S. Bogialli
Università degli studi di Padova

16.35 – 17.00-COFFEE BREAK (Giardino Napoletano)

17.00 – 17.15 – **O12-B** – *KELVIN PROBE FORCE MICROSCOPY: A QUANTITATIVE, LABEL-FREE AND HIGHLY SENSITIVE TOOL FOR ANTIGEN/ANTIBODY RECOGNITION PROCESS*

C. Di Franco, E. Macchia, L. Sarcina, L. Scandurra, L. Torsi, G. Scamarcio
CNR-Istituto di Fotonica e Nanotecnologie

17.15 – 17.30 – **O13-B** – *CELECTOR, AN INNOVATIVE INSTRUMENTATION FOR LABEL-FREE SORTING AND QUALITY CONTROL OF LIVING CELLS FOR IMPROVED THERAPY MEDICIANL PRODUCTS*

<u>B. Roda</u>, S. Zia, F. Alviano, L. Bonsi, A. Zattoni, P. Reschiglian
Università degli Studi di Bologna

17.30 – 17.45 – **O14-B** – *FFF MULTIDETECTION FOR SIZE-RESOLVED MEASUREMENTS OF DRUG RELEASE FROM PROTEIN-CONJUGATED GOLD NANOPARTICLES*

J. Wang, S. Giordani, V. Marassi, B. Roda, P. Reschiglian, <u>A. Zattoni</u>
Università degli Studi di Bologna

17.45 – 18.00 – **O15-B** – *CRISPR-CAS-ASSISTED AMPLIFICATION FOR IMPROVED MMP2 PROTEASE DETECTION VIA PEPTIDE-PNA TRANSLATOR*

<u>L. Capelli</u>, F. Pedrini, A. Di Pede, S. Fortunati, M. Mattarozzi, R. Corradini, A. Porchetta, A. Bertucci
Università degli Studi di Parma

18.30 – ASSEMBLEA (SALA / Room: PINACOTECA)

MARTEDI'-TUESDAY 19/09/2023

FOR THE WHOLE DAY: RECEIPTs RELEASE AT THE SECRETARIAL DESK

Sessione Parallela: Scienza-Separazioni-2

SALA / Room: PINACOTECA

Moderatori: Prof. Danilo Corradini; Prof. Tommaso Cataldi

09.00 – 09.45 - **PL2 - Gert Desmet (Vrije Universiteit Brussel).**

CURRENT STATE-OF-THE-ART IN COLUMN TECHNOLOGY FOR LIQUID CHROMATOGRAPHY

09.55 – 10.15 **- KN2-SP** - *MINIATURIZING SAMPLE PROCESSING: OPPORTUNITIES, CHALLENGES, AND ADVANCES*

C. Crescenzi, G. Grasso, M. Iannaccone, O. Perugini
Università degli Studi di Salerno

10.15 – 10.30 - **O7-SP** - *PIPETTE-TIP µSPE ON CARBON NANOMATERIAL FROM RICE HUSK ASH FOR DETERMINATION OF RESIDUAL FLUOROQUINOLONES IN URINE*

P. Bianchini, F. Maraschi, F. Merlo, A. Speltini and A. Profumo
Università degli Studi di Pavia

10.30 – 10.45 – **O8-SP** – *INVESTIGATION ON γ-CYCLODEXTRIN-BASED NANOMATERIALS AS SOLID-PHASE MICROEXTRACTION COATING FOR EFFICIENT EXTRACTION OF HIGH-MOLECULAR WEIGHT POLYCYCLIC AROMATIC HYDROCARBONS FROM ENVIRONMENTAL SAMPLES*

N. Riboni, F. Bianchi, M. Scaccaglia, F. Bisceglie, A. Secchi, C. Massera, P. Luches, M. Careri
Università degli Studi di Parma

10.45 – 11.15-COFFEE BREAK (Giardino Napoletano)

11.15 – 11.30 – **O9-SP** - *INNOVATIVE THERMALLY ASSISTED ON-LINE SOLID PHASE EXTRACTION-REVERSED PHASE LIQUID CHROMATOGRAPHY APPLIED TO TARGETED NUTRIMETABOLOMICS IN HUMAN BIOFLUIDS*

L. Renai, L. Marzullo, G. Bonaccorso, S. Orlandini, M.C. Bruzzoniti, M. Del Bubba
Università degli Studi di Firenze

11.30 – 11.45 – **O10-SP** - *A NEW HYDROGEL MATERIAL FOR THE ENRICHMENT OF N-LINKED GLYCOPEPTIDES*

C. M. Montone, C. Cavaliere, A. Cerrato, S. Piovesana
Università degli Studi di Roma Sapienza

11.45 – 12.00 – **O11-SP** - *EVALUATION OF THE IMPACT OF PARTICLE GEOMETRY ON THE KINETIC PERFORMANCE OF ZWITTERIONIC TEICOPLANIN-BASED CHIRAL STATIONARY PHASES*

S. Felletti, C. De Luca, G. Mazzoccanti, F. Gasparrini, M. Catani, A. Cavazzini
Università degli Studi di Ferrara

12.00 – 12.15 – **O12-SP** – *FFF-BASED MONITORING OF SURFACE AND STABILITY EVOLUTION OF AIRBORN SUBMICROPLASTICS FOLLOWING ACTIVE TRANSPORT TO BEEHIVES*

V. Marassi, L. Faccani, P. Marrazzo, B. Roda, A. Zattoni, S. Giordani, A. Zappi, I. Zanoni, A.L. Costa, P. Reschiglian
Università degli Studi di Bologna

12.15 – 12.30 – **O13-SP** - *IDENTIFICATION OF THE TIANEPTINE TRANSFORMATION PRODUCTS IN RIVER WATER BY UHPLC-MS/MS*

E. Cruz, V. Termopoli, V. Consonni, M. Orlandi, F. Gosetti
Università degli Studi di Milano Bicocca

12.30 – 12.45 – **O14-SP** – *IN-DEPTH LC-HRMS ANALYSIS OF THE EFFECTS OF CHLORINE-BASE DRINKING WATER TREATMENTS ON TOXINS PRODUCED BY CYANOBACTERIA*

A. Miglione, L. Tartaglione, M. Varra, C. Dell’Aversano, M. Simonazzi, L. Pezzolesi, F. Guerrini, R. Pistocchi, G. Graziani, I. Vasumini, A. Pandolfi
Università Federico II di Napoli

12.45 – 13.00 – **O15-SP** – *RAPID ANTIMONY SPECIATION ANALYSIS IN NATURAL WATERS VIA FRONTAL CHROMATOGRAPHY-ICP-MS*

D. Spanu, D. Monticelli, S. Recchia
Università degli Studi dell'Insubria

Sessione Parallela: Ambienti e Beni Culturali-1

SALA / Room: SALA DELLA CORNICE

Moderatori: Prof. Claudio Minero; Prof.ssa Paola Fermo

09.55 – 10.15 **– KN1-ABC** - *NON-EXHAUST EMISSION FROM ROAD TRAFFIC: CONTRIBUTION FROM FRICTION MATERIALS USED IN BRAKE PADS*

R. Santalucia, R. Depetris, G. Drago, A. Sin, F. Pellegrino, V. Maurino
Università degli Studi di Torino

10.15 – 10.30 – **O1-ABC** - *MICROWAVE-ASSISTED PRETREATMENT AND Py-GC-MS TO STUDY MICROPLASTICS AND CORRELATED POLLUTANTS*

G. Biale, J. La Nasa, L. Fiorentini, S. Giannarelli, A. Ceccarini, D. Carnaroglio, M. Mattonai, F. Modugno
Università degli Studi di Pisa

10.30 – 10.45 – **O2-ABC** – *SPECTROSCOPIC AND MULTI-SPECTRAL IMAGING FOR THE ON-SITE CHARACTERISATION OF EGYPTIAN PAINTED CARTONNAGES FROM THE AGA KHAN III NECROPOLIS, ASWAN (EGYPT)*

V. Guglielmi, P. Piacentini, A. D'Amato, C. A. Lombardi, V. Comite, A. Bergomi, M. Borelli, A. Tomaino, P. Fermo
Università degli studi di Milano

10.45 – 11.15-COFFEE BREAK (Giardino Napoletano)

11.15 – 11.30 – **O3-ABC**- *ANALYTICAL APPROACHES FOR THE DETERMINATION OF THE CONCENTRATION OF AIR POLLUTANTS IN MUSEUM ENVIRONMENTS*

M. Ricciardi, G. Fiocco, D. Sofia, M. Malagodi, O. Motta, A. Proto
Università degli Studi di Salerno

11.30 – 11.45 – **O4-ABC** - *OPTIMIZATION OF EXTRACTION AND CHARACTERISATION OF ORGANIC RESIDUES IN POTSHERDS FROM "CANTIERE DELLE NAVI ANTICHE DI PISA"*

F. Nardella, A. Giannaccini, M. Mattonai, J. La Nasa, I. Degano, G. Pace, A. Camilli, E. Ribechini
Università degli Studi di Pisa

12.00 – 12.15 – **O5-ABC** – *CHEMICAL CHARACTERIZATION OF FLINT ARCHAEOLOGICAL FINDS*

C. Chiurlia, T. Forleo, L. C. Giannossa, A. Mangone
Università degli Studi di Bari Aldo Moro

12.15 – 12.30 – **O6-ABC** - *A MULTI-ANALYTICAL APPROACH FOR THE DETERMINATION OF THE FINENESS OF 12TH-13TH CENTURY EMILIA-ROMAGNA DENARII*

G. Marussi, M. Crosera, S. Licen, S. Fornasaro, G. Carraro, B. Callegher, G. Adami
Università degli Studi di Trieste

12.30 – 12.45 – **O7-ABC** – *GEL-SUPPORTED LIQUID EXTRACTION: BUILDING A BRIDGE BETWEEN NON-INVASIVE AND LABORATORY ANALYSES FOR THE IDENTIFICATION OF DYES*

A. Bosi, A. Ciccola, I. Serafini, F. Vincenti, G. Peruzzi, V. Nigro, P. Postorino, C. Montesano, M. Sergi, R. Curini, G. Favero
Università degli Studi di Roma Sapienza

12.45 – 13.00 – **O8-ABC** – *VIS-NIR HYPERSPECTRAL METHODS AND PHOTOLUMINESCENCE MA-IMAGING SYSTEMS FOR THE ASSESSMENT AND STUDY OF THE PERFORMANCE OF NEW CLEANING SYSTEMS FOR PAINTINGS*

S. Prati, F. Ramacciotti, L. Cazals, M. Thoury, L. Bertrand, E. Catelli, G. Sciutto, R. Mazzeo
Università degli Studi di Bologna

Sessione Parallela: Green Chemistry

SALA / Room: ARCHEOLOGIA

Moderatori: Prof.ssa Alessandra Bianco Prevot; Prof.ssa Paola Donato

09.55 – 10.15 **– KN1-GC** - *THE ROLE OF ANALYTICAL CHEMISTRY IN FACING THE CHALLENGES OF BIODEGRADABLE PLASTICS*

M. Mattonai, N. Pecorelli, A. Bevilacqua, F. Marchelli, R. Ferrentino, J. La Nasa, G. Andreottola, L. Fiori, E. Ribechini
Università degli Studi di Pisa

10.15 – 10.30 – **O1-GC** - *A NEW POSSIBLE APPLICATION OF KARKADE' EXTRACT USING RAPID SOLID-LIQUID EXTRACTION (RSLDE)*

V. Nebbioso, D. Naviglio, M. Gallo, E. Di Maio, P. Trucillo
Università degli Studi di Napoli Federico II

10.30 – 10.45 – **O2-GC** – *RETENTION PROPERTIES OF A POROUS GRAPHITIC CARBON COLUMN AS STATIONARY PHASE IN SUPERCRITICAL FLUID CHROMATOGRAPHY*

P. Donato, F. Rigano, R. La Tella, P. Dugo, L. Mondello
Università degli Studi di Messina

10.45 – 11.15-COFFEE BREAK (Giardino Napoletano)

11.15 – 11.30 – **O3-GC**- *A GREEN EXTRACTION METHOD BASED ON CARBON NITRIDE SORBENT FOR THE SIMULTANEOUS DETERMINATION OF FREE AND CONJUGATED ESTROGENS IN MILK*

E. Taglioni, C. Cavaliere, A. Laganà, C.M. Montone, A.L. Capriotti
Università degli Studi di Roma Sapienza

11.30 – 11.45 – **O4-GC** - *A BIOACTIVE CHITOSAN-BASED PACKAGING FOR FOOD PRESERVATION*

R. Costa, R. De Pasquale, E. Di Salvo, L. De Maria, R. Vadalà, N. Cicero
Università degli Studi di Messina

11.45 – 12.00 – **O5-GC** - *GRAPHENE OXIDE AND CARBON NANOTUBES NANOCOMPOSITE, BASED ON RECYCLED POLYLACTIC ACID, FOR THE MAGNETIC SOLID PHASE EXTRACTION OF XENOBIOTICS FROM URINE*

L. Antonelli, E. Lucci, R. De Santo, M. Chiara Frondaroli, C. Dal Bosco, A. Gentili
Università degli Studi di Roma Sapienza

12.00 – 12.15 – **O6-GC** – *EVALUATION OF TRACE ODOUR COMPONENTS BY MEANS OF A NOVEL 3D GC SYSTEM COUPLED TO OLPHACTOMETRIC, FID AND MS DETECTION*

D. Sciarrone, L. Cucinotta, G. De Grazia, L. Mondello
Università degli Studi di Messina

12.15 – 12.30 – **O7-GC** - *RECYCLE MATERIALS BY DEVELOPING ALTERNATIVE LOW ENVIRONMENTAL FOOTPRINT SENSORS*

R. Cancelliere, Elisa Paialunga, Laura Micheli
Università degli Studi di Roma Tor Vergata

12.30 – 12-45 – **O8-GC** - *CONTINUOUS PHOTOCATALYTIC SYSTEM FOR WATER REMEDIATION: A LAB-SCALE PROTOTYPE*

C. Stevanin, M. Cescon, T. Chenet, E. Sarti, V. Costa, V. Cristino, S. Caramori, L. Pasti
Università degli Studi di Ferrara

13.00 – 14.00 - Lunch (libero)

14.00 – 15.00 – Sessione poster / Poster Session: Alimenti (P1-14); Ambiente e Beni Culturali-1 (P1-13); Equilibri (P1-5); Green-Chemistry (P1-3); Spettrometria di Massa (P1-10).

15.00 – 16.00 – ASSEMBLEE DIVISIONALI ED INTERDIVISIONALI

ROOM	**ARCHEOLOGIA**	**PINACOTECA**	**SALA DELLA CORNICE_1**	**SALA DELLA CORNICE_2**
15.00-15.30	Chemiometria	Bioanalitica	Spettroscopia analitica	Scienza delle Separazioni
15.30-16.00	Sensori		Green Chemistry	Chimica Forense

N.B. Per chi debba effettuare presentazioni nella Sala della Cornice (1 o 2), si prega di avvisare il comitato organizzatore nella sede congressuale.

16.15 – GITA SOCIALE / Guided City Tour

16.15 - Punto di ritrovo / Meeting point: Ingresso Palazzo D'Avalos.

Si raccomanda di identificare la rispettiva guida mediante il tagliandino presente nella borsa del congressista.

	GRUPPI: A, B	**GRUPPI: C, D**
16.15 - 17.45	Visita guidata della città / Guided tour of the city	Visita presso la Riserva Naturale Regionale Punta Aderci la quale verrà raggiunta in pullman / Visit of the Riserva Naturale Regionale Punta Aderci which will be reached by bus
18.00 – 19.30	Visita presso la Riserva Naturale Regionale Punta Aderci la quale verrà raggiunta in pullman / Visit of the Riserva Naturale Regionale Punta Aderci which will be reached by bus	Visita guidata della città / Guided tour of the city

20.15 – 20.45. SHUTTLE CIRCOLARI PER CENA TIPICA / Traditional dinner Shuttle

Partenza da Belvedere Romani

21.00 – CENA TIPICA. Hotel Perrozzi (Contrada, Via Buonanotte, 71, 66054 Vasto CH)

MERCOLEDI'-WEDNESDAY 20/09/2023

Sessione Parallela: Chemiometria

SALA / Room: PINACOTECA

Moderatori: Prof. Alessandro Ulrici; Prof. Davide Ballabio

09.00 – 09.45- **PL3 - Jean-Michel Roger (UMR ITAP INRAE)**.

APPLICATIONS OF NIR SPECTROSCOPY COUPLED WITH CHEMOMETRICS ON ENVIRONMENTAL AND AGRICULTURAL ISSUES.

09.55 – 10.15 - **KN1-CH** – *OPTIMIZATION OF TARGETED AND UNTARGETED METHODS USING EXPERIMENTAL DESIGN PROCEDURES: ENVIRONMENTAL AND FOOD CASE STUDIES*

C. Durante, M. Battisti, B. Benedetti, M. Cocchi, S. Pellacani
Università di Modena e Reggio Emilia

10.15 – 10.30 - **O1-CH** – *SINGLE-MOLECULE BIOELECTRONIC SENSOR: IMPROVING RELIABILITY WITH CHEMOMETRIC APPROACHES*

M. Caputo, L. Sarcina, C. Scandurra, K. Björkström, C. Di Franco, G. Frusconi, L. Haeberle, R. Österbacka, G. Scamarcio, L. Torsi, E. Macchia
Università degli Studi di Bari Aldo Moro

10.30 – 10.45 – **O2-CH** – *DATA GEOMETRY TO SOLVE CLUSTERING AND UNMIXING ISSUES*

A. Olarini, M. Cocchi, L. Duponchel, C. Ruckebusch
Università di Modena e Reggio Emilia / Université de Lille

10.45 – 11.15-COFFEE BREAK (Giardino Napoletano)

11.15 – 11.30 - **O3-CH** – *A SURVEY OF DATA FUSION STRATEGIES WITH FOCUS ON ANALYTICAL APPLICATIONS*

F. Marini
Università degli Studi di Roma Sapienza

11.30 – 11.45 - **O4-CH** – *DEVELOPMENT AND OPTIMIZATION OF UPLC-HRMS METHOD FOR METABOLOMIC CHARACTERIZATION OF MOUNTAIN DENOMINATION FOOD USING EXPERIMENTAL DESIGNS*

S. Pellacani, L. Strani, M. Cocchi, M. Battisti, C. Durante
Università di Modena e Reggio Emilia

11.45 – 12.00 - **O5-CH** – *FUSION OF DIFFERENT SPECTRAL FEATURES TO EXPLORE THE DISTINCTIVE SIGNATURES OF MOUNTAIN FOOD PRODUCTS*

L. Strani, C. Durante, S. Pellacani, J. A. Pierna, S. Michelini, V. Pizzamiglio, M. Cocchi
Università di Modena e Reggio Emilia

12.00 – 12.15 – **O6-CH** – *MULTIBLOCK METHODOLOGIES APPLIED TO MULTIOMICS DATASETS WITH CLINICAL AND DIAGNOSTIC OBJECTIVES*

V. Caponigro, S. Mires, F. Marini, E. Sommella, F. Merciai, E. Salviati, M. Basilicata, P. Campiglia, T. Dong, K.A. Eastwood, M.Caputo
Università degli Studi di Salerno

12.15 – 12.30 – **O7-CH** – *A MULTI-OMIC APPROACH COUPLED TO CHEMOMETRICS TO IDENTIFY ILLICIT STORAGE TREATMENT IN FRESH FISH*

E. Robotti, M.H. Belay, E. Barberis, M. Manfredi, A. Benedetto, P. Brizio, M. Pezzolato, M.C. Abete, E. Marengo
Università degli Studi del Piemonte Orientale

12.30 – 12.45 – **O8-CH** – *CHEMOMETRIC ANALYSIS FOR TRACEABILITY OF HIGH-VALUE ITALIAN RICE CULTIVARS: A MULTI-PLATFORM APPROACH*

M. Foschi, A. Biancolillo, C. Scappaticci, A.A. D'Archivio
Università degli Studi di L'Aquila

12.45 – 13.00 – **O9-CH** - *STUDY OF THE SOURCES OF VARIANCE IN MINIATURIZED NIR SPECTROSCOPY THROUGH ANOVA-SIMULTANEOUS COMPONENT ANALYSIS (ASCA)*

B. Giussani, C. Alamprese, S. Grassi, R. Boqué, J. Riu, G. Gorla
Università degli Studi dell'Insubria

Sessione Parallela: Sensori e Biosensori-3

SALA / Room: ARCHEOLOGIA

Moderatori: Prof.ssa Giovanna Marrazza; Prof. Stefano Cinti

09.55 – 10.15 – **KN3-SB** – *ANALYTICAL APPLICATIONS OF THE SINGLE-MOLECULE WITH A LARGE-TRANSISTOR (SiMoT) TECHNOLOGY*

E. Macchia, L. Sarcina, C. Scandurra, M. Caputo, M. Catacchio, C. Di Franco, A. Tricase, P. Bollella, G. Scamarcio, F. Torricelli, L. Torsi
Università degli Studi di Bari Aldo Moro

10.15 – 10.30 - **O16-SB** – *HIGH-PERFORMANCE SENSING APPLICATION WITH A STABLE PHYSISORBED ANTIBODIES LAYER*

C. Scandurra, L. Sarcina, C. Di Franco, M. Caputo, M. Catacchio, P. Bollella, G. Scamarcio, E. Macchia, L. Torsi
Università degli Studi di Bari Aldo Moro

10.30 – 10.45 – **O17-SB** – *MOLECULAR IMPRITED POLYMERS FOR TRACE ANALYSES OF FOOD CONTAMINANTS*

A. Tricase, M, Valentino, E, Macchia, N. Ditaranto, L. Torsi, P. Bollella
Università degli Studi di Bari Aldo Moro

10.45 – 11.15-COFFEE BREAK (Giardino Napoletano)

11.15 – 11.30 - **O18-SB** – *SYNTHETIC DNA STRANDS CONJUGATED WITH ANTIGENS AND ENZYMES FOR ULTRASENSITIVE ELECTROCHEMICAL ANTIBODIES DETECTION*

A. Díaz-Fernández, S. Ranallo, F. Ricci
Università degli Studi di Roma Tor Vergata

11.30 – 11.45 - **O19-SB** – *DYNAMIC AND REVERSIBLE DECORATION OF DNA-BASED SCAFFOLDS*

N. Farag, E. Del Grosso, F. Ricci
Università degli Studi di Roma Tor Vergata

11.45 – 12.00 – **O20-SB** – *ELECTROCHEMICAL DETECTION OF DNA THROUGH A VERSATILE MICROFLUIDIC PLATFORM*

P. S. Sfragano, M. Buchinger, S. Laschi, I. Palchetti
Università degli Studi di Firenze

12.00 – 12.15 – **O21-SB** – *PAM-ENGINEERED TOEHOLD SWITCH DNA AS ACTIVATORS OF CRISPR-CAS12A FOR SENSING APPLICATIONS*

N. Bagheri, A. Idili, A. Porchetta
Università degli Studi di Roma Tor Vergata

12.15 – 12.30 – **O22-SB** – *ELECTROCHEMICAL APTASENSOR BASED ON LASER-INDUCED GRAPHENE ELECTRODES FOR Escherichia coli DETECTION*

F. Vivaldi, L. Sembranti, A. Bonini, N. Poma, A. Carota, D. Biagini, A. Dallinger, F. Greco, A. Tavanti, F. Di Francesco
Università degli Studi di Pisa

12.30 – 12.45 – **O23-SB** – *ENTROPY DRIVEN CELL-FREE TRANSCRIPTION SENSORS*

A. Urošević, A. Idili, F. Ricci
Università degli Studi di Roma Tor Vergata

12.45 – 13.00 – **O24-SB** - *TOWARDS OPTODES FOR ALBUMIN DETECTION: EXPLORING THE COUNTLESS OPPORTUNITIES OF SULFONPHTHALEIN DYES AS RECEPTORS*

M. Guembe-Garcia, L. R. Magnaghi, A. Capucciati, G. Alberti, P. Quadrelli e R. Biesuz

Università degli Studi di Pavia

Sessione Parallela: Ambiente e Beni Culturali-2

SALA / Room: SALA DELLA CORNICE

Moderatori: Prof. Carlo Dossi; Prof. Gianpiero Adami

09.55 – 10.15 – **KN2-ABC** – *DATA FUSION BASED ON SELF-ORGANIZING MAP ALGORITHM FOR CONTEXTUALIZING ENVIRONMENTAL SAMPLING*

S. Licen, V. Bandelj, A. Bressan, S. Fornasaro, E. Greco, A.S. Gaetano, G. Adami, P. Barbieri
Università degli Studi di Trieste

10.15 – 10.30 - **O9-ABC** – *INCREASING THE ACCURACY AND THE REPRODUCIBILITY OF THE PROCESSING METHOD FOR POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLERS*

M. Baglietto, H. MacKeown, B. Benedetti, B. Cossu, C. Scapuzzi, M. Di Carro, E. Magi
Università degli Studi di Genova

10.30 – 10.45 – **O10-ABC** – *CHLORINATED AND BROMINATED PERSISTENT POLLUTANTS IN SEA TURTLES OF ADRIATIC AREA: A MULTI-RESIDUAL APPROACH*

S. D'Antonio, R. Ceci, A. De Benedictis, G. Di Bernardo, F. Di Giacinto, L. Di Renzo, M. Leva, G. Mariani, G. Scortichini, G. Diletti
Istituto Zooprofilattico Sperimentale Dell'Abruzzo e Molise "G. Caporale"

10.45 – 11.15-COFFEE BREAK (Giardino Napoletano)

11.15 – 11.30 – **O11-ABC** – *OCCURRENCE OF PER- AND POLYFLUORINATED ALKYL SUBSTANCES IN WASTEWATER TREATMENT PLANTS IN NORTHERN ITALY*

B. Giannelli Moneta, M. Cerasa, A. Laganà, C. M. Montone, S. Mosca, V. Paolini, C. Cavaliere
Università degli Studi di Roma Sapienza

11.30 – 11.45 – **O12-ABC** – *CHEMICAL CHARACTERIZATION AND SPECIATION OF THE SOLUBLE FRACTION OF ARCTIC PM10*

M. Marafante, S. Bertinetti, L. Carena, D. Fabbri, M. Malandrino, D. Vione, S. Berto
Università degli Studi di Torino

11.45 – 12.00 – **O13-ABC** – *A SIMPLE TWO-MEDIA DEGRADATION MODEL TO EVELAUATE THE ENVIRONMENTAL FATE OF 4-ISOBUTYLACETOPHENONE, A SEMIVOLATILE TRANSFORMATION PRODUCT OF IBUPROFEN*

M. Minella, C. Arsene, I. G. Bejan, C. Roman, R. I. Olariu, M. Passananti, L. Carena, C. Minero, D. Vione
Università degli Studi di Torino

12.00 – 12.15 – **O14-ABC** – *EVALUATION OF SORPTION ABILITY OF SOY PROTEIN MICROSPONGES TOWARDS* Pb^{2+} *IONS*

S. Anselmo, T. Avola, K. Kalouta, S. Cataldo, G. Sancataldo, N. Muratore, V. Foderà, V. Vetri, A. Pettignano
Università degli Studi di Palermo

12.15 – 12.30 – **O15-ABC** – *ONLINE AUTOMATED MEASUREMENT AND OPTIMIZATION OF H2O2 CONCENTRATION USING ARDUINO ROBOT*

D.Palma, K.U. Antela, A. Morales, M.L. Cervera, A. Bianco Prevot
Università degli Studi di Torino

12.30 – 12.45 – **O16-ABC** – *THERMAL DEGRADATION CHEMISTRY OF LIPIDS: AN AGEING STUDY ON EVOO SAMPLES BY MEANS OF GAS AND LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY TECHNIQUES*

V. Chiaia, G. Micalizzi, D. Donnarumma, A. Irto, C. Bretti, P. Cardiano, L. Mondello
Università degli Studi di Messina

12.45 – 13.00 – **O17-ABC** - *CHARACTERIZATION OF ORGANIC MATTER IN SOIL WITH BIOPLASTICS AND QUANTIFICATION OF AGED BIOPLASTICS BY PY-GC-MS AND EGA-MS*

A.G. Rombolà, C. Torri, I. Coralli, A. Facchin, D. Fabbri
Università degli Studi di Bologna

13.00 – 14.00 - Lunch (libero)

14.00 – 15.00 – Sessione poster / Poster Session: Ambienti e Beni Culturali-2 (P14-29); Chemiometria (P1-10); Sensori e Biosensori-2 (P13-24); Spettroscopia (P1-9).

Sessione Parallela: Chemiometria / Spettroscopia-1

SALA / Room: PINACOTECA

Moderatori: Prof.ssa Marina Cocchi; Prof. Nicola Cioffi

15.00 – 15.20 – **KN2-CH** - *DATA DIMESIONALITY REDUCTION OF HYPERSPECTRAL IMAGES FOR PEARS PUNCTURING IDENTIFICATION*

R. Calvini, V. Ferrari, C. Menozzi, P. Offermans, L. Maistrello, G. Foca, A. Ulrici
Università di Modena e Reggio Emilia

15.20 – 15.35 – **O10-CH** – *AN ANALYTICAL STRATEGY BASED ON HSI-NIR AND CHEMOMETRICS FOR THE NON-CONTACT QUANTIFICATION OF COLLAGEN IN BONES*

C. Malegori, G. Sciutto, P. Oliveri, S. Prati, S. Benazzi, E. Catelli, S. Cercatillo, D. Paleček, R. Mazzeo, S. Talamo
Università degli Studi di Genova

15.35 – 15.50 – **O11-CH** – *THE ROLE OF CHEMOMETRIC STRATEGIES IN PROCESSING MULTIBLOCK HYPERSPECTRAL DATA FOR THE SELECTIVE IDENTIFICATION OF BIOLOGICAL FLUIDS IN FORENSIC EVIDENCE*

G. Sciutto, E. Alladio, P. Oliveri, A. Mazzoleni, E. Catelli, C. Malegori, S. Prati, R. Mazzeo, M. Occhipinti, P. Garofano, R. Alberti, T. Frizzi
Univesrità degli Studi di Bologna

15.50 – 16.05 – **O12-CH** – *A NON-TARGETED APPROACH BASED ON RAMAN SPECTROSCOPY AND CHEMOMETRICS TO STUDY APULIAN AND SICILIAN TOMATOES FROM ORGANIC AND CONVENTIONAL FARMING*

T. Forleo, L.C. Giannossa, A.Mangone
Università degli Studi di Bari Aldo Moro

16.05 – 16.20 – **O1-S** – *THE IMPORTANCE OF ANALYTICAL SPECTROSCOPY IN THE FASHION INDUSTRY*

M. Innocenti, F. Biffoli, M. Bonechi, A. Comparini, E. Mariani, G. Pappaianni, M. Verrucchi, A. De Luca, W. GiurlanI
Università degli Studi di Firenze

16.20 – 16.35 – **O2-S** - *ASSESSING INTERMETALLIC DIFFUSION IN ELECTROPLATED GOLD COATINGS: A COMBINED EDS AND XRF SPECTROSCOPIC APPROACH*

W. Giurlani, F. Biffoli, I. Maccioni, C. Giovani, D. Bettoni, M. Innocenti
Università degli Studi di Firenze

16.35 – 17.00 – **COFFEE BREAK (Giardino Napoletano)**

17.00 – 17.15 – **O3-S** - *XPS ANALYSIS OF BUFFER AND CONCENTRATION EFFECTS ON DOPAMINE POLYMERIZATION FOR ONE-HEALTH APPLICATIONS*

A. Carlino, D. Chirizzi, A.R. De Bartolomeo, F. Milano, L. Giotta, M. R. Guascito
Università degli Studi del Salento

17.15 – 17.30 – **O4-S** - *XPS CHARACTERIZATION OF QDs-TiO_2 NANOCOMPOSITES FOR SOLAR FUELS PRODUCTION*

N. Ditaranto, F.S. Freyria, N. Channa, A. Fortunati, M. Zoli, S. Hernandez, N. Blangetti, M. Manzoli, S. Brovelli, B. Bonelli
Università degli Studi di Bari Aldo Moro

17.30 – 17.45 – **O5-S** - *AN ANALYTICAL APPROACH FOR CLARIFYING THE ZINC IMMOBILIZATION BY MARBLE WASTE POWDERS*

M. Fantauzzi, S. Liscia, B. Elsener, D. Biggio, D. Atzei, A. Rossi
Università degli Studi di Cagliari

17.45 – 18.00 – **O6-S** - *XPS AND ATR FTIR INVESTIGATION OF FUNCTIONALISED POLYMER SURFACE*

G. Casula, F. Zara, M. Fantauzzi, L. Brundu, B. Elsener, A. Rossi
Università degli Studi di Cagliari

Sessione Parallela: Sensori-Biosensori-4

SALA / Room: ARCHEOLOGIA

Moderatori: Prof. Marco Giannetto; Prof.ssa Ilaria Palchetti

15.00 – 15.15 – **O25-SB** - *2D NANOMATERIALS FOR BIOLOGICAL APPLICATIONS*

E. De Gregorio, N. Calisi, L. Tedeschi, N. Poma, F. M. Vivaldi, T. Lomonaco, P. Salvo
Università degli Studi di Pisa

15.15 – 15.30 – **O26-SB** – *GRAPHENE-BASED SMART INKS FOR ELECTROANALYSIS*

A. Silvestri, C. Zanardi, S. Vazques Diás, G. Misia, F. Poletti, A. Cortajarena, M. Prato
Universita Ca' Foscari Venezia

15.30 – 15.45 – **O27-SB** – *NANOMATERIAL-BASED STRATEGIES FOR ENHANCED ELECTROCHEMILUMINESCENCE BIOSENSING*

A.Zanut, A.Porchetta, F.Paolucci, G.Valenti, P. Pastore, S.Bogialli
Università degli Studi di Padova

15.45 – 16.00 – **O28-SB** – *TAILORING ZnO-BASED PIEZOTRONICS SENSORS BY CHEMICAL SPECIATION*

G. Arrabito, V. Ferrara, G. Prestopino, P.G. Medaglia, M. Scopelliti, B. Pignataro
Università degli Studi Palermo

16.00 – 16.15 – **O29-SB** - *EXPLORING THE ELECTROCHEMICAL PROPERTIES OF A NANOASSEMBLY OF CATIONIC CYCLODEXTRIN CARBON NANOTUBES AND FERROCENYL-CARNOSINE*

C. Abate, G. Neri, A. Fragoso, O. Giuffrè, C. Foti
Università degli Studi di Messina

16.15 – 16.30 – **O30-SB** – *AuNPs+TiO2 HYBRID ELECTRODES FOR THE PHOTOELECTROCHEMICAL DETECTION OF CIPROFLOXACIN*

S. Comis, D. Fumagalli, M. Longhi, V. Pifferi, L. Falciola
Università degli Studi Milano

16.35 – 17.00 – **COFFEE BREAK (Giardino Napoletano)**

17.00 – 17.15 – **O31-SB** –*LABEL-FREE IMMUNOSENSOR FOR THE DETECTION OF Pseudomonas aeruginosa IN WATER SAMPLES: STATIC AND DYNAMIC DETECTION*

E. Paialunga, R. Cancelliere, G. Sarpi, A. Ceccarelli, L. Micheli
Università degli Studi di Roma Tor Vergata

17.15 – 17.30 – **O32-SB –** *ELECTROCHEMICAL SENSORS FOR FAST DETECTION OF CANNABINOIDS IN Cannabis sativa L.*

A. Monari, G. Foca, A. Ulrici, B. Zanfrognini, V. Brighenti, F. Pellati, C. Zanardi, L. Pigani
Università degli Studi di Modena e Reggio Emilia

17.30 – 17.45 – **O33-SB** - *POINT-OF-CARE ELECTROCHEMICAL MAGNETOGENOASSAY FOR THE DETECTION OF MUTATED KRAS ONCOGENE*

S. Fortunati, C. Giliberti, A. Bertucci, V. Bianchi, A. Boni, I. De Munari, E. Ricciardi, P. Giacomini, R. Corradini, M. Giannetto, M. Careri
Università degli Studi di Parma

Sessione Parallela: Spettrometria di Massa

SALA / Room: SALA DELLA CORNICE

Moderatori: Prof.ssa Anna Laura Capriotti; Prof. Achille Cappiello

15.00 – 15.20 – **KN1-MS** - *MASS SPECTROMETRY-BASED PROTEOMICS IN THE LIFE SCIENCES: ANALYTICAL PERSPECTIVE AND NEW OPPORTUNITIES*

M. Mattarozzi
Università degli Studi di Parma

15.20 – 15.35 – **O1-MS** – *EXPLORING THE POTENTIAL OF EXTRACTIVE-LIQUID SAMPLING ELECTRON IONIZATION MASS SPECTROMETRY (E-LEI-MS) SYSTEM IN FOOD AND BIOLOGICAL APPLICATIONS*

A. Arigò, G. Nevola, G. Famiglini, P. Palma, A. Cappiello
Università degli Studi di Urbino Carlo Bo

15.35 – 15.50 – **O2-MS** – *INNOVATIVE APPROACHES FOR IMPURITY IDENTIFICATION: LIQUID ELECTRON IONIZATION INTERFACE COUPLED WITH HIGH-RESOLUTION MASS SPECTROMETRY AND NORMAL/REVERSED PHASE UHPLC*

G. Grasselli, A. Arigò, N. Marittimo, G. Famiglini, P. Palma, M. Saeed, S. Perry, P. Navarro, P. Clarke, M. Brittin, A. Cappiello
Università degli Studi di Urbino Carlo Bo

15.50 – 16.05 – **O3-MS** – *A SIMPLE DILUTION AND SHOOT: LOW-PRESSURE GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY FOR THE DETERMINATION OF PHTHALATES IN EXTRAVIRGIN OLIVE OIL*

A. Ferracane, M. Zoccali, P.Q. Tranchida, L. Mondello
Università degli Studi di Messina

16.05 – 16.20 – **O4-MS** – ON-LINE LIQUID-GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY FOR POLYCYCLIC AROMATIC HYDROCARBONS ANALYSIS IN EXTRA-VIRGIN OLIVE OIL

M. Zoccali, A. Arena, P.Q. Tranchida, L. Mondello
Università degli Studi di Messina

16.20 – 16.35 – **O5-MS** - *DEVELOPMENT OF A MASS-SPECTROMETRY-BASED APPROACH FOR THE EVALUATION OF THE MIGRATION OF ALLERGENIC PROTEINS FROM PLANT-BASED FOOD CONTACT MATERIALS*

M. Piergiovanni, L. Toma, M. Mattarozzi, O. Pitirollo, M. Grimaldi, A. Cavazza, N. Riboni, F. Bianchi, M. Careri
Università degli Studi di Parma

16.35 – 17.00 – **COFFEE BREAK (Giardino Napoletano)**

17.00 – 17.15 – **O6-MS** - *HEAT-INDUCED LIPID MODIFICATIONS IN PISTACIA VERA BY MAILLARD REACTIONS*

G. Ventura, C.D. Calvano, A. Monopoli, I. Losito, T.R.I. Cataldi
Università degli Studi di Bari Aldo Moro

17.15 – 17.30 – **O7-MS** - *MASS SPECTROMETRY ANALYSIS OF QUORUM SENSING MOLECULES IN SAMPLES FROM PATIENTS WITH SEPTIC SHOCK*

F. Dal Bello, A. Affricano, V. Fanelli, V. Cantaluppi, C. Medana
Università degli Studi di Torino

19.00 – Social Dinner Shuttle

Partenza da Belvedere Romani

20.30 – SOCIAL DINNER & BEST POSTER AWARDS

Ristorante Vistamare, presso Grotta del Saraceno Village

Via Osca, 6, 66054 Vasto CH

GIOVEDI'-THURSDAY 21/09/2023

Sessione Parallela: Spettroscopia-2 / Elettroanalitica

SALA / Room: PINACOTECA

Moderatori: Prof.ssa Barbara Giussani; Prof. Cosimino Malitesta

9.00 – 9.20 **– KN1-S** - *DEVELOPMENT AND ANALYTICAL CHARACTERIZATION OF NOVEL BIOACTIVE HYBRID COMPOSITES FOR BIOMEDICAL OR AGRI-FOOD APPLICATIONS*

S. Cometa, L. Pinto, F. Busto, A. Castellaneta, A. Marzulli, F. Baruzzi, G. Iannacone, E. De Giglio
Università degli Studi di Bari Aldo Moro

9.20 – 9.35 - **O7-S** - *PLASMONIC SENSOR FOR DETECTING CIRCULATING BIOMARKERS*

R. D'Agata, N. Bellassai, G. Spoto
Università degli Studi di Catania

9.35 – 9.50 – **O8-S** – *SPECTROSCOPIC AND MORPHOLOGICAL CHARACTERIZATION OF GREEN-SYNTHESIZED COPPER NANOPARTICLES FOR ANTIMICROBIAL APPLICATIONS*

M. C. Sportelli, R. A. Picca, D. D'Agostino, M. Izzi, N. Cioffi
Università degli Studi di Bari Aldo Moro

9.50 – 10.05 – **O9-S** – *PLGA MICELLE-STABILIZED ANTIMICROBIAL CERIUM OXIDE NANOPARTICLES INCORPORATION IN GELATINE AND MAIZE STARCH FILMS*

V. Marchianò, M. Matos, G. Gutierrez, M.C. Blanco-Lopez , N. Cioffi , N. Ditaranto
CSGI

10.05 – 10.20 – **O10-S** – *PROBING THE INTERACTION BETWEEN NANOANTIMICROBIALS AND LIPID MEMBRANES*

M. Izzi, M. Oliver, M. Miró, N. Cioffi
Università degli Studi di Bari Aldo Moro

10.20 – 10.35 – **O11-S** – *CHARGE TRANSFER ESTIMATION IN MOLECULAR CRYSTAL THROUGH RAMAN AND INFRARED SPECTROSCOPIES: A THEORETICAL STUDY*

F. Biffoli, M. Salvi, I. Cartechini, C. Fontanesi, M. Pagliai, E. Venuti, T. Salzillo, M. Innocenti
Università degli Studi di Firenze

10.35 – 10.50 – **O12-S** – *INSIGHTS IN THE ELECTROSYNTHESIS OF ZINC/CALCIUM HYDROXIDES: A SPECTROSCOPIC STUDY*

M. Izzi, D. Quarato, M.C. Sportelli, N. Cioffi, R. A. Picca
Università degli Studi di Bari Aldo Moro

10.50 – 11.20-COFFEE BREAK (Giardino Napoletano)

11.20 – 11.35 – **O1-EL** - *ANALYTICAL CHARACTERISATION OF DEPOSITS PRODUCED BY PULSED CURRENT*

E. Mariani, V. dell'Aquila, S. Bitossi, W. Giurlani, P. Lo Nostro, M. Innocenti
Università degli Studi di Firenze

11.35 – 11.50 – **O2-EL** - *ELECTRODEPOSITION AND CHARACTERIZATION OF MANGANESE ARSENIDES (MnXAs) AS PROMISING CANDIDATES IN SPINTRONICS*

G. Pappaianni, W. Giurlani, D. Morini, M. Bonechi, F. Montanari, C. Bazzicalupi, M. Innocenti
Università degli Studi di Firenze

11.50 – 12.05– **O3-EL** - *PRINTING ENZYMES AND NANOMATERIALS: WATER-BASED INK FORMULATION FOR STENCIL-PRINTING ELECTRODES*

A. Tricase, V. Marchianó, N. Ditaranto, E. Macchia, C. Di Franco, L. Gentile, D. Leech, R. Kidayaveettil, G. Scamarcio, L. Torsi, P. Bollella
Università degli Studi d Bari Aldo Moro

12.05 – 12.20 – **O4-EL** – *TOWARDS UNDERSTANDING THE ELECTROCHEMICAL BEHAVIOUR OF 3D GRAPHENE STRUCTURES: FROM SYNTHESIS TO ELECTROANALYTICAL APPLICATIONS*

A.B. Carbonaro, D. Fumagalli, V. Greco, A. Gulino, V. Pifferi, L. Falciola, A. Giuffrida
Università degli Studi di Catania

12.20 – 12.35 – **O5-EL** - *PRINT-LIGHT-SYNTHESIS OF GOLD THIN FILM ELECTRODES FOR ELECTROCHEMICAL SENSING*

S. Gianvittorio, H. Pick, D. Tonelli, A. Lesch
Università degli Studi di Bologna

Sessione Parallela: Equilibri

SALA / Room: SALA DELLA CORNICE

Moderatori: Prof. Maurizio Remelli; Prof. Carmelo Sgarlata

9.00 – 9.20 **– KN1-Eq** - *CURRENT IT TOOLS AND BEST PRACTICES FOR DETERMINATION OF STABILITY CONSTANTS FROM POTENTIOMETRIC DATA*

S. Berto, S. Blasco, L. Castellino, A. Cvetkovski, S. Gama, E. García-España, P. Hermann, V. Kubíček, G. Lando, M. Marafante, M. Meyer, W. Plass, L. Quinodoz, D. Milea
Università degli Studi di Torino

9.20 – 9.35 – **O1-Eq** - *LANTHANIDES RECOVERY, FROM AQUEOUS SOLUTIONS, BY BIOSORPTION ONTO GALDIERIA SULPHURARIA*

C. Manfredi, A.J. Amoruso, C. Ciniglia, M. Iovinella, A. El Hassanin, M. Trifuoggi
Università Federico II di Napoli

9.35 – 9.50 – **O2-Eq** – *IRON(III) COMPLEXES OF FLAVANONES IN CITRUS FRUITS: STABILITY, STRUCTURES AND ANTIOXIDANT PROPERTIES*

E. Furia, D. Aiello, L. Bartella, L. Di Donna, V. Lettera, A. Napoli
Università degli Studi della Calabria

9.50 – 10.05 – **O3-Eq** – *MULTI-TECHNIQUE CHARACTERIZATION AND SPECIATION OF OXOVANADIUM(IV)/8-HYDROXYQUINOLINE-2-CARBOXYLIC ACID AQUEOUS SYSTEM*

M. Marafante, S. Bertinetti, O. Akintola, B. Kintzel, W. Plass, S. Gama, D. Milea, S. Berto
Università degli Studi di Torino

10.05 – 10.20 – **O4-Eq** – *A MULTIANALYTICAL APPROACH TO ASSESS THE CHEMICAL SPECIATION OF CADMIUM(II) IN THE NORTH SEA*

G. Lando, N. Porcino, M. Del Core, C. De Stefano, D. Milea, M. Sprovieri
Università degli Studi di Messina

10.20 – 10.35 – **O5-Eq** – *METHOTREXATE-BASED METAL-COORDINATED ASSEMBLIES RESPONDING TO pH STIMULI: A MULTIPLE EQUILIBRIA STUDY IN SOLUTION AND AT THE INTERFACE*

G. D. G. Santonoceta, C. Sgarlata
Università degli Studi di Catania

10.35 – 10.50 – **O6-Eq** – *BE POSITIVE! MORE THAN A STATE OF MIND BEHIND THE THERMODYNAMIC STUDY OF METAL COMPLEXES WITH NOVEL CALCITERMIN PEPTIDE DERIVATIVES*

D. Bellotti, S. Leveraro, M. Rowińska-Żyrek, M. Remelli
Università degli Studi di Ferrara

10.50 – 11.20-COFFEE BREAK (Giardino Napoletano)

11.20 – 11.35 – **O7-Eq** - *INTERACTION OF THE FUNGAL METABOLITE HARZIANIC ACID WITH RARE-EARTH CATIONS*

G. De Tommaso, M. M. Salvatore, F. De Paola, M. Iuliano, A. Andolfi, M. Della Greca, F. Vinale, A. Staropoli, F. Salvatore, M. Giuda, A. Siciliano, R. Nicoletti

Università Federico II di Napoli

11.35 – 11.50 – **O8-Eq** - *GALLIC ACID FOR THE SEQUESTRATION OF ORGANOMETALS IN AQUEOUS SOLUTIONS*

A. Irto, S. G. M. Raccuia, R. M. Cigala, C. Bretti, O. Gómez-Laserna, P. Cardiano, C. De Stefano, F. Crea
Università degli Studi di Messina

11.50 – 12.05– **O9-Eq** - *HYDROXYPYRONES FOR OXOVANADIUM(IV) COMPLEXATION*

R. Cappai, A. Fantasia, D. Sanna, G. Sciortino, F. Pisanu, E. Garribba, M. A. Santos, V. M. Nurchi
Università degli Studi di Sassari

12.05 – 12.20 – **O10-Eq** – *MEDIUM AND IONIC STRENGTH DEPENDENCE OF FORMATION CONSTANTS. THE "PURE WATER" MODEL*

C. Bretti, P. Cardiano, R.M. Cigala, F. Crea, A. Irto, G. Lando, D. Milea, C. De Stefano
Università degli Studi di Messina

12.20 – 12.35 – **O11-Eq** - *SPECIATION STUDY OF Cu(II) WITH LACTIC ACID AND PYRUVIC ACID IN SEAWATER-LIKE CONDITIONS*

R. Di Pietro, M. González-Dávila, J.M. Santana-Casiano, P. Cardiano, G. Lando, C. De Stefano
Università degli Studi di Messina

Sessione Parallela: Alimenti

SALA / Room: ARCHEOLOGIA

Moderatori: Prof. Peter Tranchida; Prof. Giampiero Scortichini

9.00 – 9.20 **– KN1-ALI** - *THE POTENTIAL OF AMBIENT MASS SPECTROMETRY COMBINED WITH CHEMOMETRICS FOR THE ASSESSMENT OF FOOD AUTHENTICITY*

F. Rigano, D. Mangraviti, C. Cafarella, P. Dugo, L. Mondello
Università degli Studi di Messina

9.20 – 9.35 – **O1-ALI** - *MULTIFUNCTIONAL PROPERTIES OF SHORT- AND MEDIUM-CHAIN PEPTIDE MIXTURES FROM HEMP SEED AGAINST METABOLIC SYNDROME*

S. E. Aita, A. Cerrato, A. Laganà, C. Lammi, C.M. Montone, A. L. Capriotti
Università degli Studi di Roma Sapienza

9.35 – 9.50 – **O2-ALI** – *FORMULATION OF BITTERS AND FOOD SUPPLEMENTS STARTING FROM EXTRACTS OF PLANT BLENDS (CONVENTIONAL PROCESS) AND BLENDING EXTRACTS OF SINGLE PURE PLANTS*

V. Nebbioso, F. Varchetta, A. Perrone, L. Avolio, E. de Martino, M. Gallo, D. Naviglio
Università Federico II di Napoli

9.50 – 10.05 – **O3-ALI** – *DETECTION OF PERFLUOROALKYL COMPOUNDS IN FOOD MATRICES: ANALYTICAL ISSUES AND FUTURE CHALLENGES*

M. Leva, S. D'Antonio, A. De Benedictis, G. Di Bernardo, G. Diletti, G. Romeo, G. Scortichini, G. Tammaro, R. Ceci
Istituto Zooprofilattico Sperimentale Dell 'Abruzzo e Molise "G. Caporale"

10.05 – 10.20 – **O4-ALI** – *DEVELOPMENT OF A μ-SPE METHOD FOLLOWED BY UPLC-MS/MS ANALYSIS FOR THE DETERMINATION OF PHOMOPSIN A IN RAW LUPIN SAMPLES*

F. Eugelio, S. Palmieri, E. Oliva, A. Pepe, F. Fanti, M. Del Carlo, D. Compagnone, M. Sergi
Università degli Studi di Teramo

10.20 – 10.35 – **O5-ALI** – *A GREEN AND INNOVATIVE APPROACH BASED ON COLLOIDAL ANALYSIS TO ASSIST WINE GROUPING*

N. Kassouf, S. Giordani, A. Zappi, D. Melucci, B. Roda, A. Zattoni, P. Morozzi, P. Reschiglian, V. Marassi
Università degli Studi di Bologna

10.35 – 10.50 – **O6-ALI** – *IDENTIFICATION AND QUANTIFICATION OF COENZYME Q10 AND VITAMIN K1 IN BRASSICA MICROGREENS AND BABY LEAVES BY LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY COUPLED WITH ATMOSPHERIC PRESSURE CHEMICAL IONIZATION*

M. Bianco, I. Losito, B. Leoni, P. Santamaria, C.D. Calvano, T. R. I. Cataldi
Università degli Studi di Bari

10.50 – 11.20-COFFEE BREAK (Giardino Napoletano)

11.20 – 11.35 – **O7-ALI** - *NUTRITIONAL VALUE OF HOUSE CRICKET (Acheta domesticus) FED DIETS SUPPLEMENTED WITH DIFFERENT LEVELS OF THE SEAWEED Palmaria palmata IN THE FEEDING MEDIA*

B. Ajdini, I. Biancarosa, G. Cardinaletti, S. Illuminati, A. Annibaldi, F. Girolametti, M. Fanelli, G. Pascon, M. Martinoli, C. Truzzi
Università Politecnica delle Marche

11.35 – 11.50 – **O8-ALI** - *NIAS MIGRATION STUDY FROM POLYMERIC MATERIAL TO DRY FOOD*

M. Roncoli, M. Ferretti, E. Perin, V. Gianotti
Università degli Studi del Piemonte Orientale

11.50 – 12.05– **O9-ALI** - *SINGLE-LABORATORY VALIDATION OF THE ThRAll METHOD FOR MULTIPLE ALLERGEN DETECTION IN CHOCOLATE*

R. Pilolli, A. Lamonaca, C. Nitride, E. De Angelis, C. van Poucke, N. Gillard, A.-C. Huet, M. De Loose, J. Henrottin, E.C.N. Mills, L. Monaci
CNR-ISPA

12.40 – 13.10 – Chiusura convengo / Closing Ceremony & Best Oral Awards

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POSTER

LUNEDI-MONDAY 18/09: 14.00 – 15.00 – Sessione poster: Bioanalitica-Omics (P1-6); Forense, Tossicologia e Salute (P1-10); Scienza delle Separazioni (P1-17); Sensori e Biosensori-1 (P1-12); Elettroanalitica (P1-7).

MARTEDI-TUESDAY 19/09: 14.00 – 15.00 – Sessione poster: Alimenti (P1-14); Ambiente e Beni Culturali-1 (P1-13); Equilibri (P1-5); Green-Chemistry (P1-3); Spettrometria di Massa (P1-10).

MERCOLEDI-WEDNESDAY 20/09: 14.00 – 15.00 – Sessione poster: Ambienti e Beni Culturali-2 (P14-29); Chemiometria (P1-10); Sensori e Biosensori-2 (P13-24); Spettroscopia (P1-9).

Cod.	**Titolo**	**Autore presentante**
	Alimenti	
ALI-P1	QUALI-QUANTITATIVE CHARACTERIZATION AND VALORIZATION OF SOLID AND LIQUID WASTES FROM EVO AGRIFOOD CHAIN	M. Locatelli
ALI-P2	CHEMICAL PROFILING AND ANTI-INFLAMMATORY/ANTI-LIPOGENIC ACTIVITY OF AN ARTICHOKE STEM EXTRACT	R. Sardella
ALI-P3	DETERMINATION OF 289 PESTICIDES IN ITALIAN EGGS FROM LARGE RETAIL: ORGANIC vs CONVENTIONAL PRODUCTION	R. Rosato
ALI-P4	UNTARGETED VOLATOLOMICS BY HEADSPACE MICROEXTRACTION GAS CHROMATOGRAPHY-MASS SPECTROMETRY (HS-SPME-GC-MS) FOR THE IDENTIFICATION OF QUALITY MOLECULAR MARKERS IN FRESH-CUT ICEBERG LETTUCE	G. Spadaccino
ALI-P5	CHARACTERIZATION OF VOLATILE COMPOUNDS IN ITALIAN CIDER USING GC×GC-MS AND MULTIVARIATE ANALYSIS	C. Orecchio
ALI-P6	HS-SPME/GC–MS AND CHEMOMETRIC APPROACH FOR THE STUDY OF VOLATILE PROFILE IN X-RAY IRRADIATED SURFACE-RIPENED CHEESES	R. Zianni
ALI-P7	A HIGH-SENSITIVE ANALYTICAL METHOD FOR THE DETERMINATION OF PAHS IN INFANT FOOD	A. Chiappinelli
ALI-P8	SYNTHESIS OF MOLECULARLY IMPRINTED POLYMER (MIP) FOR THE SELECTIVE EXTRACTION OF PHYTOSTEROLS IN FOOD MATRICES	E. Oliva
ALI-P9	LIPIDOMICS AND METABOLOMIC TOOLS FOR THE CHARACTERIZATION OF CAMEMBERT CHEESE ANALYSED BY UHPLC-Q-ORBITRAP-MS	M. Campaniello
ALI-P10	CHARACTERIZATION OF HELIX ASPERSA ASPERSA FLAVOUR: NUTRITIONAL AND POLLUTION EVALUATION	F. Saiano
ALI-P11	INTEGRATED ANALYTICAL APPROACH FOR THE CHARACTERIZATION OF BIO-BASED FOOD CONTACT MATERIALS	M. Mattarozzi
ALI-P12	RICE HUSK AS A SUSTAINABLE SOLUTION FOR SOIL REMEDIATION: FEASIBILITY AND PRACTICAL APPLICATION	R. Cecire
ALI-P13	ADVANCING MOSH/MOAH ANALYSIS TOWARDS SPECIATION AND CONTAMINANT IDENTIFICATION	A. Miliazza
ALI-P14	FAST SYNTHESIS OF MOLECULARLY IMPRINTED POLYMERS FOR THE DETERMINATION OF AFLATOXINS IN SUPPLEMENT FOODS	S. Palmieri
	Ambiente e Beni Culturali	

ABC-P1	ANALYTICAL-PETROGRAPHIC STUDY OF BUGNATO DEGRADATION OF AN ANCIENT MILAN BUILDING	M. Tomassetti
ABC-P2	LEACHATE FROM LANDFILL OF MUNICIPAL SOLID WASTE: CHARACTERIZATION AND DETERMINATION OF THERMODYNAMIC PROPERTIES	C. Alessandrello
ABC-P3	PYRENE REMOVAL FROM WATER BY NEW ADVANCED UP AND DOWN PHOTOCATALYST	S. Barreca
ABC-P4	ASSESSING SOURCES AND FRACTIONS OF METALS ASSOCIATED WITH BEACHED PLASTIC LITTER: A CASE STUDY IN LAKE COMO (ITALY)	S. Carnati
ABC-P5	ON THE BEHAVIOR OF DISPERSED MICROPLASTICS IN LEAD - CONTAMINATED WATERS	A. Pettignano
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S-P5	SIMPLE COLORIMETRIC ASSAY BASED ON POLYMERS NANOFILMS FOR GOLD DETECTION	S. Scarano
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EL-P3	VOLUMETRIC POWER OUTPUT OF GLUCOSE/O2 FULLY PRINTED ENZYME-BASED BIOFUEL CELL	S. D'Ingeo
EL-P4	CATECHOL-BASED LIGANDS FOR IRON SPECIATION IN SEAWATER: STABILITY AND ELECTROCHEMICAL ANALYSIS	G. Roncoroni
EL-P5	STUDY OF ELECTROCHEMICAL SENSORS BASED ON MULTI-WALLED CARBON NANOTUBES (MWCNTs) AND BT2T4 OLIGOMERS FOR ENANTIOMERIC DISCRIMINATION.	S. Comis

EL-P6	FUNCTIONAL PROPERTIES OF HYDROGEN PERMEATION BARRIERS ON STEEL	R. Hannachi
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Plenary Speakers

PL1

Jiří Homola

Institute of Photonics & Electronics,
Czech Academy of Sciences

PL2

Gert Desmet

Vrije Universiteit Brussel

PL3

Jean-Michel Roger

UMR ITAP INRAE

PL1

ADVANCES IN PLASMONIC AFFINITY BIOSENSORS FOR MEDICINE

J. Homola

Institute of Photonics & Electronics, Czech Academy of Sciences

This presentation is devoted to plasmonic affinity biosensors and the main challenges related to their use in medical diagnostics. The selected advances in plasmonic biosensor research that aim to address some of these challenges are also discussed[1]. These include advances in plasmonic nanostructures and instrumentation, microfluidic systems, functional materials, and detection assays. Examples of medical applications to be discussed include plasmonic biosensors for the diagnosis of Myelodysplastic syndromes (MDS) and renal system disorders[2].

References:

1. H. Altug, S.H. Oh, S.A. Maier, J. Homola, Nature Nanotechnology, 17, 5–16 (2022).
2. T. Špringer, Z. Krejčík, J. Homola, Biosensors and Bioelectronics 194, 113613 (2021).

PL2

CURRENT STATE-OF-THE-ART IN COLUMN TECHNOLOGY FOR LIQUID CHROMATOGRAPHY

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Considering the current versatility of physicochemical conditions (GC, (U)HPLC, SFC, High-temperature LC,…) and support formats (open-tubular columns, fully porous or core-shell particles, silica and polymer monoliths, micro-machined columns,…), each with their own propagators, the chromatographic community would benefit a lot if the speed and efficiency data obtained on these systems could be compared in a system- and geometry-independent plot, directly showing the time needed to achieve a given degree of efficiency or peak capacity or resolution.

The kinetic plot method, mathematically not more demanding than establishing a Van Deemter curve, offers this possibility. The method uses two simple mathematical equations, well-rooted in the basic theory of chromatography and only requires a set of experimental van Deemter data as the input. In the present contribution, the audience will be taken through the few steps (only involving a few multiplications and divisions) needed to establish kinetic plots. Subsequently, it will be shown how this method can easily be extended from isocratic LC to any type of gradient operation and to GC and SFC. Subsequently, a series of examples, taken both from own experiments and recent literature, will be given to demonstrate how kinetic plots can be used to compare the different chromatographic systems in each category (GC, SFC, LC) as well as mutually comparing the speed characteristics of LC with those of SFC and GC.

Another advantage of the kinetic plot representation, i.e., that it can be used to unambiguously assess the packing quality of given column without having to measure or define a characteristic length or mean particle size will be illustrated as well by comparing the intrinsic packing performance of a number of state-of-the art LC columns packed with fully-porous and core-shell particles.

In addition, kinetic plots can also be used to compute and visualize the difference in peak capacity and required time between 1D-LC and on-line and off-line 2D-LC.

PL3

APPLICATIONS OF NIR SPECTROSCOPY COUPLED WITH CHEMOMETRICS ON ENVIRONMENTAL AND AGRICULTURAL ISSUES

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ITAP/ChemHouse, INRAE, France

Of all the spectrophotometric techniques, near infrared spectroscopy (NIRS) offers an interesting compromise between light penetration and chemical absorption. In addition, agricultural and environmental issues require the assessment of complex, heterogeneous products made up of numerous chemicals. NIRS is therefore a natural choice as one of the main non-destructive and rapid methods for dealing with agricultural and environmental issues. However, the NIRS is sensitive to many physical and chemical factors. The spectra measured are therefore highly complex, and NIRS requires the use of chemometric techniques to predict concentrations, recognise classes or identify compounds.

This presentation will illustrate the use of NIRS coupled with chemometrics, based on three complementary examples. The first will present the design of a waste sorting machine, which required a variable selection chemometrics method. The second will focus on an application of hyperspectral imaging to characterise the wood composition of a whole slice of eucalyptus, using a new methodology combining spatial and spectral analysis with a multi-block approach. The third part will illustrate the detection of diseases on grapevine leaves using hyperspectral images coupled with a multi-curve resolution methodology.

Keynotes

COLORIMETRIC LABELS IN LATERAL FLOW IMMUNOASSAYS: CAN WE OVERCOME THE USE OF NOBLE METAL NANOPARTICLES?

F. Di Nardo, S. Cavalera, L. Anfossi, C. Baggiani

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In 2022, the global immunoassays market in term of revenue was estimated to be worth $40.2 billion, and almost the half ($20.5 billion) was accounted by the lateral flow immunoassay (LFIA)[1].

Considering the future of LFIA we can identify two clear trends, one is much more "ultra-sensitivity, more complex, integrated" and the other is "simple and convenient". Strategies to achieve the ultra-sensitivity in LFIA usually exploit fluorophores and chemiluminescent molecules but have disadvantages like requiring additional steps, additional chemicals and different detection methods that rely on the use of detectors or readers making the analysis more complicated, expensive, and time-consuming.

These aspects have discouraged the market entry of the more complex LFIAs that mainly remain as laboratory prototypes (except for some fluorescent-based LFIAs).

To maintain the simplicity of the colorimetric-LFIA, in the last years huge efforts have been devoted to evaluating the use of alternative colorimetric labels instead of the most used gold nanoparticles[2,3].

In this presentation an overview on the most recent colorimetric strategies will be critically discussed, pointing out the use of new colorimetric labels that may overcome the use of the traditional noble metal-based labels.

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KN1-SP

VIEWS ON THE USES OF COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY-MASS SPECTROMETRY IN FOOD ANALYSIS

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Comprehensive 2D gas chromatography (GC×GC) was first described in 1991[1], and stemmed from the revolutionary work made by J.B. Phillips. When GC×GC is used in combination with a mass spectrometer (GC×GC-MS), it forms an extremely powerful three-dimensional system. Often excessively powerful, with it being more spectacular than being a true necessity (in analytical terms) in several instances.

The present lecture will provide critical views on the use of GC×GC-MS within the context of food analysis. Focus is devoted to the GC×GC-MS literature covering the period 2018-2023, even though the conclusions made are general ones. In fact, even though the use of GC×GC in food analysis has a publication history of nearly 25 years, it has never gained a firm hold in this applicational field, in neither the industry nor in academia. Possible reasons for such a lacking, along with current analytical challenges for which specific GC×GC-MS configurations would certainly be useful, are provided.

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KN1-B

COMPREHENSIVE GCxGC HIGH RESOLUTION MS AND SELECTIVE ISOLATION OF CHEMICALS IN THE INVESTIGATION OF HUMAN CHEMOSIGNALS ELICITED FROM EMOTIONAL STIMULATION

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An update from the Potion project, which is investigating compositional changes of sweat volatiles in 49 volunteers undergoing fear stimulation to demonstrate the existence of human chemosignals affecting the emotional state of a receiver[1]. Upon collection from apocrine sweat glands in the armpit by pre-treated pads, chemicals were collected and then extracted, enriched, and trapped into Tenax GR tubes by dynamic headspace (DHS) at 60°C. Analyses were carried out by comprehensive two-dimensional gas chromatography (GCxGC) and time-of-flight mass spectrometry (TOF), whereas emotions were induced by immersing individuals wearing portable sensors (EDA, ECG, respiratory rate) in virtual reality scenarios[2]. Emotional rankings showed the successful induction of fear. Out of 364 detected compounds (311 identified, 38 assigned to class, 15 true unknowns), a subset of 319 sweat volatiles showed significantly different concentration values compared to field pad blanks (fold change FC > 3.0, $p_{.FDR} < 0.05$) [3] and 19 were significantly increased during fear vs. relaxed condition (FC > 2.5, $p_{.FDR.BH} < 0.05$, with paired t-tests). Out of these, 8 chemicals were commercially available and selected as safe for olfactory experiments on human volunteers. We could detect 3 of these 8 chemicals by real time mass spectrometry (proton transfer reaction – time of flight, PTR-TOF), and show abrupt increases in concentration when volunteers experienced intense fear in the virtual scenario. Lab-made modifications of the GCxGC setup allowed to selectively isolate a number of sweat volatiles (including unknowns) for additional olfactory experiments with human volunteers[1].

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KN2-SB

MOLECULAR IMPRINTING AND SENSING TECHNOLOGY: A HAPPY MARRIAGE BASED ON ETSABLISHED AND INNOVATIVE STRATEGIES

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One effective strategy to obtain tailor-made synthetic receptors is to use the molecular imprinting technique, which gives rise to molecularly imprinted polymers (MIPs)[1], termed also chemical antibodies for highlighting their recognized ability to act as antibody mimics endowed with specific molecular recognition properties analogous to those of natural antibodies. One of the most successful MIPs application is sensing technology, where they revealed their ability to detect an incredibly wide spectrum of analytes, from small molecules, which were mostly templated at the beginning of the imprinting technology, to protein antigens, which have nowadays a well-known clinical relevance acting as biomarkers in several diseases, thus making their detection in biological samples highly relevant and useful in both diagnostic and prognostic biomedicine.

Here we present an overview of MIPs we prepared by different approaches for the imprinting of several targets, namely surface-imprinting electropolymerization[2,3], light-mediated polymerization and vapor-phase polymerization[4], and their successful use in the assembly of electrochemical and optical sensors. Particular emphasis will be given to a very innovative imprinting strategy developed for enabling the controlled and reliable MIP synthesis in any nanostructures, which represents a key factor for further extending flexibility in MIP synthetic strategies and in their integration with different kinds of transducers. Challenges and results will be discussed evidencing the advantages provided by the adopted room temperature vapor-phase polymerization in comparison with conventional liquid-phase polymerization.

The successful application of the developed imprinting approaches to the detection of proteins and drugs will be presented, giving a special focus to perspective applications in the design of bioresorbable optical sensors for *in-vivo* diagnostic applications.

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This work was partially funded by the European Union Horizon Europe program under grant agreement No 101046946 (RESORB).

KN1-FT

ADVANCED ANALYTICAL STRATEGIES FOR DETECTION OF FORENSIC RELEVANT COMPOUNDS

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The increased diffusion of New Psychoactive Substances (NPS) needs rapid screening methods for their chemical identification as early as possible after their appearance in the market. This is an important issue in forensic field and analytical chemistry, representing an objective of primary importance for health and safety at National[1], European[2] and International[3] levels.

In 120 years of activity and progression of the Forensic Science Service in the Italian National Police - *Polizia Scientifica*, the detection of illicit drugs and in general substances of abuse is evolved following the evolution of the threats given by illicit market. This path has seen the Police chemists to switch from Toxilab kits (TLC-based drug screening kits) to the instrumental techniques such as GC-FID and GC-MS. Now the challenge of identifying unknown substances, e.g. NPS continuously appearing on the illicit market, required further progresses and the use of even more performing techniques such as (U)HPLC with High Resolution Mass Spectrometry (HRMS).

This project started by considering known molecules as well as the latest reported and most concerning NPS. As an example, in the last year Italian law enforcements have reported in many seizures the presence of LSD derivatives, benzodiazepines analogues, arylcyclohexylamines or tryptamines, detected by means of UPLC-HRMS. The main challenge in recognizing NPS lies in their dynamic nature, in the continuous synthesis and introduction on the market of new drugs, mainly based on similar structures to existing ones. In these studies chemometric tools have demonstrated to be very useful to take important steps forward in the analysis and recognition of NPS.

A comprehensive approach could complete the identification where the accurate masses and ion fragmentation are not exhaustive; the availability of benchtop NMR allowed its use also in routinary quali-quantitative analysis[4]. All analytical data are collected into the national early warning system coordinated by National Institute of Health (so called SNAP-ISS) and they are shared with the collaborative centers included into the national network and with the analogue European Early Warning System.

Moreover, another goal was the increase the number of seizures and so different analytical tools could be very useful for this purpose. HERMES project[5], for example, involved the use of handheld Raman in postal parcels checking to detect drugs of abuse immediately before their diffusion and consumption.

The multidisciplinary nature of the activities needs integrated approaches to be tailored for effective results in the fight against illicit drugs.

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KN2-B

SIMILAR BUT NOT IDENTICAL: THE HUNT FOR BINDING COOPERATIVITY IN ARTIFICAL ANTIBODIES

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Molecularly imprinted polymers (MIPs) are synthetic materials obtained by polymerization in presence of a template target molecule that are able to rebind selectively to this target. MIPs in the form of nanoparticles prepared by solid phase synthesis (nanoMIPs) are virtually free of residual template, characterized by high affinity and selectivity for the target molecule, easy to graft onto solid surfaces and fully compatible with the aqueous environment. Thus, they have the potential to be low-cost and robust alternatives to natural antibodies in applications as immunoassay, sensoristics and complex sample purification by affinity chromatography.

NanoMIPs and polyclonal antibodies are assumed to share the same binding behaviour, with very similar thermodynamic and kinetic properties, due to the presence of mutually independent binding sites and characterized by a continuous distribution of the binding affinity with respect to an average value. Nevertheless, there are scattered experimental indications suggesting the possibility of a different binding behaviour, where nanoMIPs could show positive cooperativity. As positive cooperativity would have repercussions on the practical use of nanoMIPs, the demonstration of the existence of such binding behaviour is of significant practical relevance.

With this goal in mind, recently our research group embarked in the study of the binding behaviour of a model system, represented by fluoroquinolone-imprinted nanoMIPs. This communication discuss the strategy used in investigating the existence of such behaviour, starting from the definition of binding isotherm models compatible with a cooperative behaviour in a system characterized by a multiplicity of binding sites, passing through the approach used to obtain robust experimental data to conclude with an critical examination of the statistical reliability of the results obtained that show the net prevalence of binding isotherm models consistent with positive cooperativity.

KN2-SP

MINIATURIZING SAMPLE PROCESSING: OPPORTUNITIES, CHALLENGES, AND ADVANCES

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In recent decades, significant advancements in analytical instrumentation have achieved instrumental detection limits far below the requirements for most commonly targeted analytes. In response, the downsizing of sample sizes and treatment approaches has emerged as a compelling strategy to reduce costs and minimize solvent and materials consumption. Beyond cost reduction, downscaled sample treatment offers a range of advantages, including faster and simplified sampling procedures and decreased expenses related to sample manipulation and storage. Moreover, a smaller sample offers the potential for innovative analytical approaches and integrated devices for sample pre-treatment and accurate analyte determination. These opportunities hold the key to developing sustainable analytical procedures. However, the use of micro samples poses challenges beyond mere method optimization, particularly in terms of representativeness, extraction efficiency, robustness and reproducibility.

This study addresses these challenges by presenting an overview of the most successful or promising microextraction techniques for liquid samples as both, active and passive sampling, followed by the results of a comparative investigation on conventional micro solid phase extraction (μSPE) and Micro Extraction by Packed Sorbent (MEPS). The experiments were performed using four different sorbent materials and two different extraction approaches. Exemplary analytes with a wide range of polarity and chemical-physical properties were used as test samples.

The results shed light on the feasibility and limitations of the two investigated active sampling approaches and a few theoretical aspects that are frequently overlooked.

By elucidating the opportunities, challenges, and advances in miniaturized sample processing, the aim of this presentation is to provide valuable insights and guidelines into the development of robust analytical MEPS and μSPE protocols.

KN1-ABC

NON-EXHAUST EMISSION FROM ROAD TRAFFIC: CONTRIBUTION FROM FRICTION MATERIALS USED IN BRAKE PADS

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With the implementation of stricter controls on Exhaust Emissions, Non-Exhaust Emissions (NEEs), such as Volatile Organic Compounds (VOCs) and Particulate Matter (PM), have become increasingly significant, constituting a greater fraction of total vehicle emissions. Among NEEs sources, brake wear can significantly contribute to VOC and PM emissions. Tribochemical and Tribomechanical interaction between pads and rotors converts the vehicle kinetic energy into heat, leading to gradual wear of the contacting components and the release of brake dust[1]. Electric Vehicles (EVs) tire and brake wear remain the primary source of NEEs, as frictional brakes remain vital for emergency braking[2]. NEEs emissions from braking systems can vary depending on factors such as vehicle type, brake pad material, and maintenance[3]. In particular, during braking events, the high temperatures reached (600°C-800°C) can cause the thermal degradation of phenolic resin (PR), commonly used in friction materials as binder, resulting in the release of hazardous organic compounds[4]. Current research is moving toward the development of ecofriendly binders as good alternatives to PR in terms of mechanical and tribological properties[5]. There is a significant correlation between the degradation of PR, brake wear, and the formation of the tribolayer at the pad/disc interface[6,7]. Our research aims to optimize brake materials to enhance performance and safety by exploring alternative friction materials. In this context, our recent study highlights the potential 2-D materials as modifiers to tune friction and wear[8]. We also aim to gain a deeper understanding of the interactions between PR and inorganic materials present in brake pads formulations to develop ecofriendly friction materials. Pyrolysis-GC-MS technique have revealed that the presence of certain inorganic compounds in brake composite, can contribute to increased benzene emissions.

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Acknowledgements:

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KN1-GC

THE ROLE OF ANALYTICAL CHEMISTRY IN FACING THE CHALLENGES OF BIODEGRADABLE PLASTICS

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Biodegradable plastics (BPs) are a worldwide diffused commodity, mainly used to produce short-lived goods such as bags and disposable tools. While the aim of BPs is to be degraded when they leave usage, no BP is universally degradable, and specific environmental conditions are required for each material. In addition, not enough information is often available to end users on how best to dispose of BPs. This leads to mismanagement of end-of-life BPs, defying the potential advantage of these materials over conventional plastics[1]. New, informed policies are required to regulate the production, usage, and disposal of BPs, especially considering that technologies in this field are rapidly evolving.

Analytical chemistry plays a fundamental role in this framework. Innovative approaches with high-throughput characterisation techniques are necessary to obtain information on BPs' properties and their lifecycle in different environments and conditions. An advancement in understanding the degradation mechanisms of BPs and the resulting products is also needed, both in the open environment and under controlled conditions such as those of industrial plants[2]. Degradation products should be carefully considered both for their potential ecotoxicological effects and in view of possible valorisation strategies.

Based on the current state of the art, an overview of the analytical challenges posed by the current scenario on the diffusion and fate of BPs will be provided. Results will also be presented on the characterisation of the solid and liquid fractions obtained from BPs after hydrothermal treatment (HT). HT has been recently addressed as a promising pre-treatment method to improve the anaerobic digestion of BPs. HT was capable of quantitatively hydrolyse BPs into the original monomers, providing a platform for their valorisation and thus possibly improving the life cycle of BPs.

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KN1-CH

OPTIMIZATION OF TARGETED AND UNTARGETED METHODS USING EXPERIMENTAL DESIGN PROCEDURES: ENVIRONMENTAL AND FOOD CASE STUDIES

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Targeted and untargeted approaches have been extensively introduced and successfully applied across various research fields, owing to significant instrumental advancements achieved in recent years, which have notably improved their sensitivity and selectivity. Furthermore, the availability of different data analysis tools has facilitated the extraction of valuable information from acquired data, enabling comprehensive data interpretation and analysis1. However, it is of utmost of importance to prioritize the optimization of analytical methods capable of identifying and quantifying the highest possible number of chemical compounds in both targeted and untargeted analyses. Despite the importance of employing Experimental Design planning2 to achieve optimal responses with minimal experimental trials, challenges persist in determining the appropriate factors to be optimised, their level of variability, and the desired responses. This selection process remains an ongoing issue that requires careful consideration. Therefore, in this presentation, comprehensive workflows for the optimization of analytical methods based on liquid chromatography-mass spectrometry (LC-MS) will be shown in relation to two different cases of study. The first involves the determination of 33 polar emerging contaminants (encompassing pharmaceuticals, personal care products and other compounds.) in wastewater. The second case focuses on the determination of indicators (‘identity markers’) capable of distinguishing mountain foods from homologous ones. Multivariate data analysis (PCA, ROI-MCR and PLS) is also utilized to determine the optimal conditions based on multiple response variables, including peak resolution, signal intensity and analysis time.

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KN3-SB

ANALYTICAL APPLICATIONS OF THE SINGLE-MOLECULE WITH A LARGE-TRANSISTOR (SiMoT) TECHNOLOGY

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Technologies for diagnosis, monitoring, personalized treatment, as well as therapeutic response evaluation of progressive pathologies such as tumors or viral infections, are considered strategically important in Analytical Chemistry. Often, marker analysis is performed on tissues or fluids from affected organs, which can be too invasive. In this scenario, it becomes crucial to develop devices that enable minimally invasive or non-invasive analysis of peripheral biological fluids such as saliva, urine, or plasma.

Currently, there are not commercially available immunometric methods capable of testing at a single-molecule level. On the other hand, antigen-based point-of-care (POC) methods are extremely common, providing rapid and cost-effective results but with significantly lower performance, especially in terms of limit-of-identification (LOI) and reliability.

A new portable technology called Single-Molecule with a Large-Transistor (SiMoT) has been invented and developed, which can detect a single protein, a single virion, a bacterium, and even a single copy of DNA in 0.1 mL of a blood, saliva, or cystic pancreatic fluid sample (concentration = 10^{-20} mole/L). The invention is based on a transistor that integrates a layer of 10^{12} antibodies or DNA probes adsorbed onto a millimeter-sized gate. Such a detecting interface is a trillion times larger than the single molecule to be detected. The SiMoT single-sensor technology has been validated as a multipurpose platform successfully assaying the following biomarkers and pathogens: Immunoglobulin M (IgM), IgG, C-Reactive Protein (CRP), p24 protein of the HIV-1 virus capsid (p24-HIV-1), Spike1 (S1), Mucin 1 (MUC1), Interleukin 6 (IL-6), CD55, KRAS, microRNA, COVID-19, Xylella fastidiosa. The key elements, such as sensing materials, FET-structures, and target molecules and the analytical figures of merit of wide-field bioelectronic sensors will be critically discussed. Moreover, the amplification effects enabling extremely sensitive large-area bioelectronic sensing will be also addressed.

The SiMoT technology, as part of the activities of the Regional Single-Molecule Digital Assay Center, is currently being employed in a clinical study involving 1,000 patients in collaboration with the IRCCS Giovanni Paolo II Oncology Hospital in Bari and the University of Brescia.

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KN2-ABC

DATA FUSION BASED ON SELF-ORGANIZING MAP ALGORITHM FOR CONTEXTUALIZING ENVIRONMENTAL SAMPLING

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Real-time or quasi-real-time instruments/sensors allow the collection of high-frequency data, moreover modern analytical techniques with a high level of automation allow to process of many samples for multi-pollutant analysis purposes in a short time interval[1,2]. Thus, the most modern direction in environmental analysis is to gather desired information from data sets of a big-data domain, containing information about a variety of physical-chemical characteristics related to each collected sample. Several different chemometric approaches are available for data mining and fusion. Among the unsupervised methods, Self-Organizing Map (SOM) algorithm[3] is an artificial neural network that can be used for exploratory data analysis and pattern recognition and can handle non-linear problems. The SOM is also able to deal with big data sets with the possibility of visually exploring the outcomes of the model in versatile 2D maps in which similar samples are mapped close together on a grid[4]. As a rule, the SOM can be built using the real-time data, thus its outcome is a matrix containing recurrent profiles that can be considered recurrent "states" of the environmental compartment. The profiles can be easily characterized by the modeled values (weight of nodes) of the monitored parameters. The output matrix can be further analyzed by clustering algorithms (e.g. k-means or hierarchical clustering) for obtaining few recurrent "macro-states" of the environmental compartment[5,6]. The obtained "macro-states" can been used for contextualizing the results obtained by spot sampling carried out for *ex-situ* lab analysis of pollutants. The sparse samplings can be contextualized considering the "macro-states" occurring before and during the sampling time for identifying samples collected during stable or unstable compartment conditions. Moreover outliers can be easily detected and interpreted[6]. Some examples concerning air and water compartments will be presented.

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DATA DIMESIONALITY REDUCTION OF HYPERSPECTRAL IMAGES FOR PEARS PUNCTURING IDENTIFICATION

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For practical applications of Near Infrared Hyperspectral Imaging (NIR-HSI) systems it is often necessary to acquire hundreds or even thousands of images to obtain robust and reliable models. Consequently, it is mandatory to apply data dimensionality reduction (DDR) methods to gain relevant information from such big data arrays. Often to face this issue the average spectrum is used, but this implies losing information about spectral variability within each image, which is the key advantage of HSI. To face this issue we proposed the hyperspectrograms approach, a DDR method which consists in converting each image of the dataset into a signal obtained by merging in sequence the frequency distribution curves of pixel-related features derived from Principal Component Analysis (PCA)[1]. According to the problem, PCA can be either calculated on each single image (Single Space Hyperspectrograms, SSH) or globally considering a common PC space (Common Space Hyperspectrograms, CSH). The hyperspectrograms are then collected in a matrix of signals, which in turn can be analysed using classical chemometric methods to simultaneously evaluate all the images of the dataset for the development of multivariate models. This approach has been recently applied to the identification of puncturing damages on pears due to *Halyomorpha halys*, an insect pest causing severe economic losses to pear growers in Italy[2]. To this aim, punctured and sound pear samples were collected in an organic orchard and acquired in the 1156-1674 nm spectral range for a period of 6 weeks from harvesting, obtaining a final dataset of 1968 hyperspectral images. Combining the hyperspectrograms approach with image level classification and feature selection using interval Partial Least Squares – Discriminant Analysis (iPLS-DA), it was possible not only to discriminate between sound and punctured pear samples but also to visualize back into the original image domain the selected features. In this manner it was possible to identify in an automated and objective manner the Regions of Interest (ROIs) of punctured areas, which will be used for further development of pixel-level classification models coupled with spectral variable selection.

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HALY.ID project of ERA-NET Cofund ICT-AGRI-FOOD, with funding provided by national sources (Ministero delle politiche agricole e forestali, MIPAAF) and co-funding by the European Union's Horizon 2020 research and innovation program, Grant Agreement number 862671

KN1-MS

MASS SPECTROMETRY-BASED PROTEOMICS IN THE LIFE SCIENCES: ANALYTICAL PERSPECTIVE AND NEW OPPORTUNITIES

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Mass spectrometry (MS)-based proteomics has emerged as a widely effective means for the identification, characterization, analysis of protein expression levels and quantification of proteins that are integral components of processes essential to life, with major implications also for forensic science[1-4]. In this context, MS-based proteomics has recently attracted the attention of forensic scientists and pathologists owing to its potential to answer different questions and face new analytical challenges with protein-based forensics[1,5]. As for clinical proteomics, the discovery of diagnostic, prognostic and predictive biomarkers, which are associated with the clinical outcome and follow-up, is experiencing a trend towards minimally-invasively collected samples to expand potential and accessibility to screening programs[6]. Furthermore, since allergies are a major health concern worldwide, MS-based food proteomics holds great promise for addressing the burning questions of allergenic risk assessment for known food sources, novel foods and new food processing strategies and their impact on the allergenicity of individual food proteins.

Since the birth of proteomics science in the '90, the number of sample preparation methods has grown exponentially, making a huge contribution to the knowledge in life sciences. Emerging technologies such as micro- and nanoscale chromatography, ion mobility separations coupled with MS, ambient-MS[7] and imaging-MS[8] show significant promise for both targeted and untargeted proteomic analysis, enabling increased depth of proteome coverage.

In this context, the continuous expansion of the application range of MS-based proteomics will be discussed together with the progress and innovation of methodological approaches.

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DEVELOPMENT AND ANALYTICAL CHARACTERIZATION OF NOVEL BIOACTIVE HYBRID COMPOSITES FOR BIOMEDICAL OR AGRI-FOOD APPLICATIONS

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The challenge posed by bacterial antibiotic resistance is a huge health problem and the use of alternative antimicrobial systems often poses an issue related to their potential toxicity. Hybrid organic-inorganic composites represent interesting systems for the development of new architectures for different emerging applications, due to their manifold opportunities to optimize the performances of their starting components. In this respect, many plant extracts have been investigated worldwide as potential sources of novel antimicrobial compounds, as alternative tools for the treatment of infectious diseases or as agents able to promote food and cosmetic preservation. On the other hand, natural compounds are often highly unstable, not soluble in aqueous solutions, susceptible to oxidation, thermal degradation and/or rapid volatilization. Among the different protection strategies, caged or lamellar clay minerals have been proposed as vehicles of natural molecules for various applications such as food packaging, hygienic-sanitary, pharmaceutic, agricultural, etc. In this respect, in the last decades we developed and characterized different clays (such as bentonite, zeolite, hydrotalcite, diatomaceous earth, etc.) modified with plant-derived organic molecules showing enhanced antibacterial, antioxidant or biocompatible properties for biomedical or agri-food applications[1-3]. More recently, a special attention was paid to the development of hybrid systems based on carvacrol or thymol, the main antimicrobial molecules composing several essential oils, loaded in Zn-exchanged montmorillonite or Zn-exchanged zeolite, designed as new antimicrobials for food packaging applications. Combination of different analytical techniques (XPS, FT-IR, TGA, GC-MS) allowed us to ascertain the success of the ion exchange process, to estimate the loading of the active molecules in the hybrid composites as well as their release in appropriate simulating media. Antimicrobial assays carried out against spoilage and pathogenic bacterial strains, showed intriguing antimicrobial activity for the proposed hybrid materials paving the way for interesting applications of these systems in the agri-food and biomedical fields.

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CURRENT IT TOOLS AND BEST PRACTICES FOR DETERMINATION OF STABILITY CONSTANTS FROM POTENTIOMETRIC DATA

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Among the participants of COST Action CA18202 NECTAR, a survey was conducted regarding what software is used daily to define stability constants from equilibrium data. The results show a high diversity in the software used, associated with a common dissatisfaction concerning the user experience. A critical evaluation of the software actually available for the analysis of potentiometric data was conducted, in order to identify the strengths and weaknesses of each of program and to use this knowledge for the development of the new IT products. With this aim, various software[1-7] were tested on an artificial dataset corresponding to six different titrations of a hypothetic hexaprotic acid with pre-set protonation constant values. Moreover, the data analysis was carried out including some errors in the input data in order to stress their impact on the refined parameters. The stability constants were determined and, the obtained results were analysed and discussed.

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This publication 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, www.cost.eu, https://cost-nectar.eu/).

KN1-ALI

THE POTENTIAL OF AMBIENT MASS SPECTROMETRY COMBINED WITH CHEMOMETRICS FOR THE ASSESSMENT OF FOOD AUTHENTICITY

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Although chromatographic methods coupled to mass spectrometry (MS) are commonly employed to elucidate the chemical composition of food matrices and assess their genuineness, they are time consuming and often require considerable efforts for method optimization and data processing. In addition, a laborious and tedious sample preparation could be necessary for single chemical classes, thus making challenging a comprehensive and exhaustive chemical characterization.

In order to face such drawbacks and introduce more competitive tools against fraudulent activities, in the last decade different fast fingerprinting analytical methods were applied for the reliable identification of "precious" foodstuffs. Among them, Ambient Mass Spectrometry (AMS) attracted special interest due to the absent or minimal sample preparation, since the sample is analyzed in its native form under ambient conditions. Moreover, AMS techniques often lead to a complete profile in a single analysis.

Within this context, the present contribution aims to describe the potential of two different AMS approaches combined with chemometrics for the fast and reliable identification of different food products, many of them labeled with PDO (protected designation of origin) trademark or preserved by slow-food associations.

In particular, Rapid Evaporative Ionization Mass Spectrometry (REIMS) and Direct Analysis in Real Time (DART) were used and compared in terms of prediction rate, as well as false positive occurrence. The first was coupled to a high-resolution tandem mass analyzer (Q-TOF) for a detailed and reliable identification of single molecular components, while the second one to a single quadrupole mass analyzer, less sophisticated, but more compact and competitive in terms of robustness and costs. The REIMS technique makes use of a surgical handpiece for the manual sampling of different matrices, while the DART approach exploits several automated sampling devices for the analysis of a multitude of samples in few minutes. The spectra obtained with each technique were collected in a spectral database and used for the building of multivariate statistical models, which allowed for the real-time identification of food samples and their differentiation based on geographical origin, trademark and genetic aspects, through a dedicated software.

Premio Giovane Ricercatore

CHEMOMETRICS: THE KEY TO UNRAVEL COMPLEX ANALYTICAL CHEMISTRY DATA

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Chemometrics, an interdisciplinary field embracing chemistry, statistics, mathematics, and data analysis, has arisen as a powerful ally within Analytical Chemistry and it has revolutionized the way we interpret and leverage data in analytical applications. This presentation examines into the pivotal role of Chemometrics as a potent weapon in unraveling intricate data complexities, and unveiling data patterns that would otherwise remain hidden. In this context, multi-way methods and multi-block approaches have emerged as particularly appreciated tools in handling complex data structures, providing enhanced insights and facilitating deeper understanding of interrelationships within multi-dimensional datasets, and, therefore, they will take center stage as the core theme of this presentation.

Furthermore, real-world case studies that show how Chemometrics has led to breakthroughs in various analytical fields, including pharmaceuticals, food safety, and clinical chemistry, enhancing the comprehension of complex systems, through its ability to identify trends, and the detection of the most meaningful features for the solution of analytical problems, will be discussed.

While Chemometrics indeed wields great power, it comes with its drawbacks and limitations. These aspects will be addressed to highlight best practices and avoid potential pitfalls, particularly when applying multi-way and multi-block techniques.

In conclusion, this talk aims to shed light on the indispensable role of Chemometrics in Analytical Chemistry, unlocking the full potential of analytical data, leading to more informed decisions and advancements across scientific disciplines.

Oral Sensori e Biosensori

O1-SB

DECORATED DNA-BASED SCAFFOLDS AS LATERAL FLOW BIOSENSORS

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In the last decades significant advances in the development of lateral flow assays have been achieved. Numerous examples for the detection of antibodies, viruses and bacteria, with high sensitivity and specificity, have been described. Despite this, new approaches to create lateral flow platforms with increasing versatility and applicability are needed. DNA nanotechnology allows the design of devices, systems and structures that can be engineered with nanometric precision. Thanks to the high programmability and specificity of non-covalent hydrogen bond base pairings, synthetic nucleic acid strands (i.e DNA) have emerged as ideal materials that can find application in a variety of fields, such as diagnostic, sensing, bioimaging and drug delivery.

In response to this, we show a novel strategy to build lateral flow assays that employ decorated DNA nanostructures as functional scaffolds to generate a readout signal upon the recognition of specific targets. The use of functional DNA scaffolds coupled with lateral flow assays allows to reach several advantages. First, the assembly of DNA structures displaying functional groups of different nature (i.e. small molecules and fluorophores) allows to employ them to generate a fluorescent readout signal only upon the recognition of the specific target. Second, the possibility to introduce different recognition elements enables the detection of diagnostic targets, ranging from antibodies to small molecules or proteins. Finally, we show the possibility to develop an assay for the simultaneous detection of multiple targets even in more complex matrices.

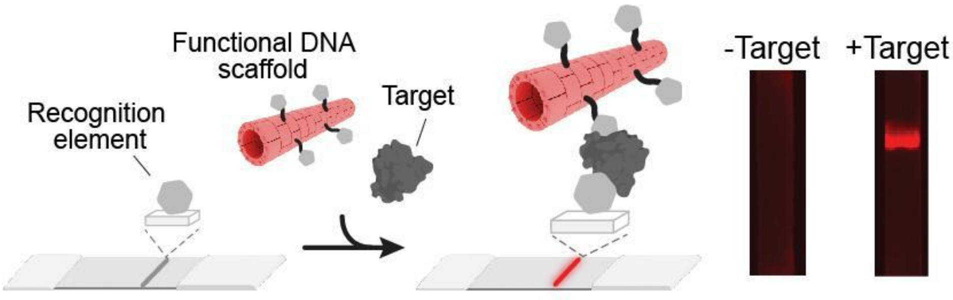

Figure 1: Scheme of a sandwich format of a LFA that employs functional DNA scaffolds as both reporter tags and recognition elements.

O2-SB

ALL-IN-ONE PAPER-BASED MICROFLUIDIC DEVICE FOR PARACETAMOL ELECTROANALYSIS IN ENVIRONMENTAL MATRICES

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Since 2020, human pharmaceuticals were included in the list of emerging contaminants from the UNESCO and their detection and elimination were incorporated in the 2030 Agenda for Sustainable Development Goal Targets[1]. Among these, analgesic and antipyretic drugs are the most widely used drugs worldwide and, despite their advantages, unused or expired pharmaceuticals are a potential source of water pollution. Paracetamol is one of the most common drugs used for analgesic and antipyretic purposes and has been found to have a much higher concentration in water streams in many European countries, even though there is not a specific regulation for the discharge limit of paracetamol, so efficient monitoring is necessary[2]. Considering the need of having integrated devices without the need of complex/expensive analytical procedures, an all-in-one paper-based fluidic system, able to detect paracetamol, has been developed. An ad-hoc paper-based testing area, coupled with a channel has been designed and wax-printed. Successively an electrochemical transducer has been scree-printed, and the whole system has been applied for the detection of paracetamol in wastewaters (prior and after the filtration system), without a specific pre-treatment of the sample. The choice of the device has been optimized in terms of type of substrate used for printing, microfluidic paper strip length/width, loading of reagents, and combination of them in a whole paper-based system, able to detect paracetamol in the matrices tested in few seconds, with detection limit down to micromolar range. The integrated device shows great promise for simple, fast, sensitive, and sustainable detection of paracetamol.

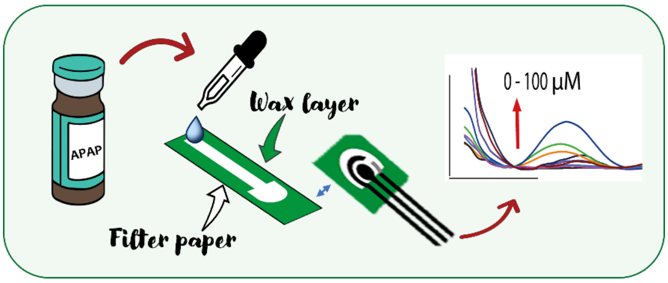

Figure 1: Schematic representation of paracetamol detection workflow on the paper-based integrated device.

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A PAPER-BASED ELECTROCHEMICAL APTASENSOR FOR USER-FRIENDLY THROMBIN DETECTION IN BIOLOGICAL MATRICES

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Thrombin (TB) is a serine protease and plays a key function in pathological and physiological coagulation, blood vessel haemostasis and wound healing. Numerous research findings suggest that TB, as a protease activating multiple receptors, exerts its effects on the onset and development of many vascular diseases, cancer cell migration and Alzheimer's disease;[1–3] thus the physiological level of TB should be carefully evaluated to avoid health complications.

Nowadays, most of the known approaches to measuring TB are based on clot formation, such as prothrombin time, activated partial thromboplastin time and TB time. However, these methods can only reflect the overall clotting capacity of the blood, but not the content of TB alone[4]. Therefore, it is of clinical relevance to develop a rapid and accurate method for monitoring TB levels. To this regards, biosensors might represent a valid alternative. In particular, due to the existence of an oligonucleotide aptamer that is selective to TB recognition, the development of colorimetric, fluorometric and electrochemical aptasensors are wide reported in literature[5–7]. The recognition is based on the formation of a G-quadruplex structure, consisting of two G-tetrads connected by two laterals TT and central TGT loops, that is able to bind TB with high affinity[8,9]. However, among the different transduction mechanisms, the electrochemical one offers the advantage to work in coloured/turbid matrices without significative interferents[10]. In this work, a paper-based electrochemical aptasensor has been designed, characterized and applied towards the detection of TB. The architecture has been characterized by the presence of gold nanoparticles (AuNPs) and a TB-aptamer labelled with a redox mediator, namely Methylene Blue (MB). The aptasensor has been designed as a "signal off" platform, in fact in presence of TB the reduction of MB at the electrode is lowered. In order to obtain the optimal performance, all the experimental parameters have been considered, i.e. substrate (polyester, paper), amount of AuNPs, probe length, probe structure, electrochemical parameters. The analytical performance has been evaluated in standard solution, serum and whole blood, yielding a detection limit in the low nanomolar range and a repeatability of ca. 10% (measured ad the relative standard deviation). The results appear promising, characterized by a far-reaching impact for clinical TB detection in terms of easiness, production time, sensitivity and cost.

O3-SB

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O4-SB

3D PAPER-BASED ELECTROANALYTICAL DEVICE FOR ALL-IN-ONE CARBARYL ANALYSIS

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Carbaryl (CBR) represents one of the most used pesticides in crop production and, due to the risks associated with its ingestion, the European Commission has established maximum levels (MRL) in food leading to the need for accurate methods for its determination. This presentation aims to propose a 3D pop-up paper/graphene-based device (3D-PP) for enzyme-free CBR analysis. The device is composed of a nitrocellulose-based sensor equipped with reduced graphene oxide (rGO) and a 3D paper pop-up enclosing different analysis steps. Both device components were obtained using a CO_2-laser plotter; the 3D-PP components were finished employing low-cost benchtop instruments (i.e., cutter plotter and wax printer) and strategies (i.e., stencil printing). The conceived 3D-PP integrates the analyte pre-concentration/purification (Fig. Ai), the hydrolysis to form an electrochemically detectable species (Fig. Aii), the neutralization of the measuring medium after the pop-up folding (Fig. B-C), and the electrochemical measurement (Fig. D). The proposed 3D-PP was challenged for the CBR determination in model solutions and different grain samples (i.e. soft wheat, durum wheat, and barley). The dose-response curve resulted linear between 1.5-33 μM, and the LOD obtained (0.4 μM) ensures the CBR determination at the MRL level (2.5 μM). Quantitative and reproducible recoveries (93-109%, RSD<6%; n=3) were obtained for different grains largely used for food production. In conclusion, a fully paper-based all-in-one device was developed exploiting benchtop, affordable and solvent-free strategies. The 3D-PP has been successfully used for CBR determination, demonstrating sensitivity, selectivity, and robustness allowing the direct analysis in different grain samples.

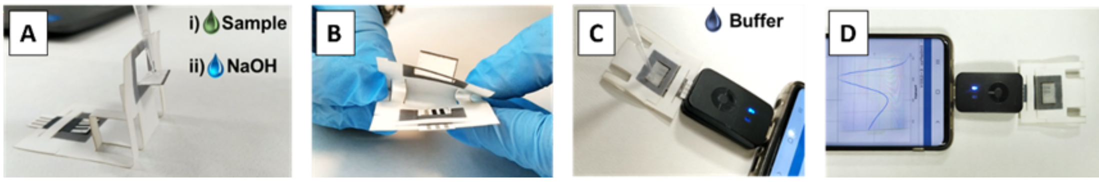

Figure 1. (**A**) sample loading on the sampling window (i) and alkaline hydrolysis (ii); (**B**) 3D pop-up folding; (**C**) neutralization of the measuring medium containing the hydrolyzed analyte; (**D**) electrochemical measurements via DPV.

Acknowledgements:

S.F. and D.C. acknowledge the Ministry of Education, University and Research (MIUR) and European Social Fund (ESF), act. I.1 "innovative doctorates with industrial characterization" for the PON R&I 2014–2020 (CCI 2014IT16M2OP005). This research was funded by the European Union – Next Generation EU. Project Code: ECS00000041; Project CUP: C43C22000380007; Project Title: Innovation, digitalization and sustainability for the diffused economy in Central Italy – VITALITY

BUTTERFLY-LIKE PAPER-BASED MICROFLUIDC POTENTIOMETRIC WEARABLE SENSOR FOR DEHYDRATION MONITORING DURING PHYSICAL ACTIVITY

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Real-time information about patients' health status is a hot topic in current medical research activities. Indeed, the future vision is to move from hospitals to home-spitals approach, in order to improve the healthcare system[1]. Technological advances are boosting this important transition, enabling the downsizing of sensing equipment, replacing bulky instrumentation, removing uncomfortable wire connections, and delivering straightforward data-transferring procedures based on wireless transmission[2]. Herein, we report an innovative wearable sensor based on potentiometric screen-printed electrodes and butterfly-like paper-based microfluidics for continuous monitoring of pH and Na^+ in sweat during physical activity for dehydration monitoring. In detail, the butterfly-like configuration allows for the sampling of fresh sweat instantly with the removal of old sweat from the sensing zone, ensuring accurate punctual biomarker analysis in sweat. Two ad-hoc modified miniaturised screen-printed sensors were embedded in a butterfly-like paper-based device for the simultaneous detection of the above-mentioned biomarkers. Furthermore, in order to fabricate a wearable system for easy analysis and data transmission, the sensing system was integrated with a portable and miniaturized potentiostat, exploiting Bluetooth data transmission. The device has been tested in standard solution obtaining calibration curves described by the following equations $y = (0.056 \pm 0.002)\ x + (0.300 \pm 0.004)$, $R^2 = 0.993$, and $y = (-0.080 \pm 0.004)\ x + (0.81 \pm 0.02)$, $R^2 = 0.983$, for Na^+ and pH respectively. Finally, the effectiveness of the developed device has been assessed by on-body real-time measurements.

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SUSTAINABLE EXTRACTION AND ANALYSIS OF ZINC IN SOIL BY COMBINING A 3D-PRINTED ANALYTICAL TOOL AND PAPER-BASED SCREEN-PRINTED SENSORS

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Zinc is an essential trace element for plants, animals, and humans. Over the last few years, insufficient levels of Zinc in agricultural soils (e.g., < 10 mg/Kg) have been related to micronutrient deficiency in the human diet[1]. At the same time, zinc levels above threshold concentrations (e.g., 150 mg/Kg) have been revealed across several European agricultural areas (i.e., 18% of the arable lands), due to mining, industrial activities, and animal manure[2]. The monitoring of Zinc in the soil becomes thus important to ensure the production of high-quality food while avoiding polluting amounts of zinc. Conventional analysis typically requires a multi-step analytical protocol, including zinc extraction and zinc analysis by laboratory-based instrumentation (e.g., atomic absorption spectroscopy). Here, we developed an analytical approach that combines Zn^{2+} extraction from soil and its analysis with a smart and green analytical methodology. We designed a customized 3D-printed device for zinc extraction from soil inspired by the method of the Community Bureau of Reference (BCR)[3] for Zn^{2+} extraction. In detail, an extraction chamber was printed by stereolithography 3D printing. The soil sample (e.g., 0.1 g) is placed inside the chamber and an extraction solution (e.g., 6 mL of 0.11 M acetic acid) is injected using a syringe. The analysis of extracted Zn^{2+} is carried out in square wave anodic stripping voltammetry with a paper-based screen-printed sensor, on which a bismuth film is previously electrodeposited ex situ. Preliminary results obtained for different soil samples showed promising analytical performance in terms of linear range (i.e., 0.1-5 ppm), LOD (i.e., 0.03 ppm), and good agreement with reference analytical methods (i.e., standard BCR extraction coupled with atomic absorption spectroscopy). Differently from the standard mineralization approach for soil analysis, which determines the total content of zinc in soil, our methodology reveals the zinc exchangeable fraction from the total content of zinc, namely the most available fraction for assimilation by vegetables. Thanks to the use of non-toxic reagents and eco-friendly materials (i.e., paper), our approach represents a green analytical method that combines the extraction and the analysis of Zn^{2+} in soils for fast and cost-effective monitoring.

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O7-SB

MOLECULARLY IMPRINTED NANOGELS IN OPTICAL SENSING

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Molecularly imprinted nanoparticles (nanoMIPs) are nanosized biomimetics prepared by means of a template assisted synthesis that coveys, to the nanomaterial, selectivity towards a targeted analyte.[1] NanoMIPs stay as the polymer-based alternative to natural antibodies and receptors, displaying similar affinities and selectivities, while offering robustness and improved stability to temperature and solvents. For these reasons, optical sensors based on nanoMIPs have been gaining significant interest.[2,3]

The effect of playing on the nanoMIP's compositions, so to entail certain defined characteristics to the nanoMIPs, such as deformability or fluorescence, will be discussed in light of the advantages in optical sensing.

It was demonstrated that soft MIP-nanogels undergo deformation of the polymeric network at binding. When coupled to surface plasmon resonance such deformation produced an enhancement of the optical signal that enabled to detect attomoles of target analyte.[3]

The combination of non-specific deformable nanogels, with a characteristic responsive behaviour, and plasmonic optical probes was studied as a mean to provide specific sensing.[4] At the plasmonic interface, the nanogels exhibited more freedom's degrees, i.e. the real-time monitoring of the refractive index variations of the surrounding medium and the time-related volume-to-phase transitions correlated to the surrounding's physical chemistry, whose combination enabled to discriminate solvents in the environment.

When fluorescent reporters are entailed to nanoMIPs, these become nanosensors apt to time-resolved fluorescence spectroscopy interrogation and demonstrating picomolar sensitivity.

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BIO-INSPIRED POLYMERS FROM ENDOGENOUS NEUROTRANSMITTERS: TOWARDS UNIVERSAL PROTEIN IMPRINTING?

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The replacement of antibodies (Abs) in bioanalytical chemistry and diagnostics (including immune-based therapeutics) with new technologies based on Animal-Friendly Affinity reagents is a long-lasting dream in the scientific community for both technological and ethical reasons, as recommended by the 2010/63/EU Directive on the protection of animals used for scientific purposes. However, despite the many attempts in this direction, Abs remain almost the only choice to address most of the (bio)analytical issues based on biomolecular recognition. In this frame, mimetic receptors appear promising, ideally guaranteeing high stability and long shelf-life, reduction of batch-to-batch variability and cost production, also covering the need for receptors for toxic and non-immunogenic targets. Strongly convinced by our recent results (1-13), we have great expectations about a class of bio-inspired polymers with high potential to function as Abs. They derive from the self-polymerization of the endogenous neurotransmitters (NTs) dopamine, norepinephrine, and serotonin. This peculiar class of "soft" Imprinted Bio-Polymers (IBPs) are temperature resistant, reusable, tunable in size and optical properties. Moreover, they are endogenous, safe, biocompatible, biodegradable, and low cost. Up to now, selected NTs-based IBPs have shown to be able to imprint almost any kind of aa-based epitope template under the same experimental conditions, from short peptides up to immunoglobulins. This opens new horizon to universally imprint any kind of peptide sequence, from a single starting monomer, which undoubtedly would represent a revolutionary achievement in affinity receptors production. Here we report an overview of the most recent results obtained by coupling polyNTs-based IBPs to biosensing, and the effective *in silico* strategies to design and optimize their performances.

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Acknowledgments:

Authors thank the Italian Ministry of Health for funding within the call "Research and training/information 2020 program on drugs, medical substances, and practices that can be used for doping purposes and for health protection in sporting activities" and the Project 'Biocompatible molecularly imprinted polymers as alternative to antibodies-based therapy for rheumatoid arthritis treatment (MIPRA)', funded by Fondazione Roche per la Ricerca Indipendente. The authors also thank the Italian Ministry of University and Research (MUR), for the project "Dipartimenti di Eccellenza 2018–2022".

O9-SB

ECO-FRIENDLY PREPARED MOLECULARLY IMPRINTED POLYMERIC NANOPARTICLES IN SENSOR DESIGN FOR THE ELECTROCHEMICAL DETERMINATION OF AMOXICILLIN

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Amoxicillin (AMOX) is a semisynthetic beta-lactam antibiotic, derived from penicillin, and used in the treatment of various bacterial infections. AMOX falls into the category of "emerging contaminants" since the excessive clinical utilization and widespread distribution in the environment due pharmaceutical industrial effluents, as well as the inefficiency of wastewater treatments in drugs degradation. Currently, SPE-HPLC/HRMS is the conventional suggested method to monitor drugs, and specifically this target from wastewater samples. As an alternative, electrochemical sensors can be applied to this aim. In particular, biomimetic receptors such as the molecularly imprinted polymers (MIPs) are today widely used for sensor development, allowing the design of highly sensitive, selective and stable recognition systems comparing to those employed in biosensors. MIPs are based on the imprinting technology, which relies on the preparation of recognition cavities onto a polymeric network complementary to specific functional groups of the imprinted target. Among synthesis methods, the polymerisation in water (MilliQ) could represent an eco-friendly strategy in MIP preparation, obtaining very stable and highly performing water-suspendable nanoparticles [1]. In this work, the preparation of nanosized MIPs (nanoMIPs) for the selective determination of AMOX in water matrices is reported. The polymerisation mixture in MilliQ water contains the eco-friendly N-isopropylacrylamide (NIPAM), acrylic acid (AA), N-(3-Aminopropyl) methacrylamide hydrochloride (NAPMA) as functional monomers, in the presence of the N-methylenebisacrylamide (BIS) and N-t-butylacrylamide (TBAm) as cross-linkers. For nanoMIPs preparation, 1 mM of amoxicillin trihydrate (AMOX) was added, acting as the template. Polymerisation reaction in water phase was carried out for 1 h at RT (in dark). 10 MW filter cartridge centrifugal tubes were used for elution process and to remove unreacted monomers (x6, 3700 rpm, 15 min). The obtained nanoMIPs (and nanoNIPs) were concentrated, characterised, and further immobilised onto functionalised screen-printed gold electrode (SPAuE) surface for sensor development. Differential pulse voltammetry (DPV) measurements were accomplished towards increasing concentration of AMOX dissolved in Britton-Robinson buffer (pH 7) in the range of nM/µM. The developed sensors exhibited amplified electrochemical responses in comparison to NIP (no analytical responses were detectable).

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O10-SB

A GUANOSINE-DERIVED SUPRAMOLECULAR HYDROGEL WITH PEROXIDASE-LIKE ACTIVITY AS A NEW TOOL FOR HYDROGEN PEROXIDE DETECTION

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Chemiluminescence (CL) is a widely used method for the quantification of hydrogen peroxide (H_2O_2), due to its high sensitivity, ease of use, and low cost. The most widely employed system is based on horseradish peroxidase (HRP) and luminol. H_2O_2 plays an important role in various applications and is a crucial biomarker in monitoring various diseases and disorders, including diabetes, cancer, cardiovascular and neurodegenerative disorders. Additionally, H_2O_2 is produced in reactions catalysed by numerous oxidase enzymes, such as glucose oxidase, alcohol oxidase, cholesterol oxidase, lactate oxidase, and glutamate oxidase[1]. Hydrogels have gained great interest in the development of biosensors, owing to their high biocompatibility and the ability to incorporate foreign substances while preserving a benign environment for the biosensing events[2]. The 3D porous structure of hydrogels increases the surface area of the material, allowing the loading of large amounts of biorecognition elements, better accessibility and a more biocompatible environment provided by the flexible and aqueous nature of hydrogels. The preservation of the native structure of biomolecules is a crucial requirement for feasibility, specificity and sensitivity in biosensing applications[2]. A CL hydrogel was prepared by simultaneous incorporation of luminol and hemin into the scaffold of a guanosine-derived hydrogel. The self-assembled hydrogel consisted of K^+-stabilized hemin/G-quadruplex structures, showing significant peroxidase-like activity to H_2O_2-mediated oxidation of luminol[3]. After adding H_2O_2, the CL signal is generated and lasts for several minutes. The long-lasting CL emission of hydrogel was achieved due to a mechanism of slow-diffusion-controlled heterogeneous catalysis. This soft biomaterial can also be used for the indirect detection of glucose, upon incorporation into the hydrogel of glucose oxidase, which produces H_2O_2 upon oxidation of glucose. As proof of concept for the development of a biosensor that uses hydrogel as a matrix for glucose detection, the CL signal has also been acquired via smartphone, using a 3D printed dark box.

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O11-SB

A VERSATILE APPROACH FOR ACHIEVING METAL ION MEDIATED INTERACTIONS ON POROUS SILICON INTERFEROMETERS

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Nanoporous silicon (nPSi) is largely used for the design of different (bio)sensing platforms due to its peculiar optical properties as interferometer and to additional beneficial aspects as the straightforward fabrication and low cost, which allows mass production of cheap (bio)sensors to be envisaged[1,2]. However, one key condition for PSi-based interferometers to work as robust and reliable sensing devices is that their surfaces should be properly functionalized to achieve a stable interaction with the analyte(s) to be optically detected[1]. To this aim, several strategies have proposed in literature, often consisting in the anchoring of a biorecognition element responsible for the selective binding with the target molecule[1,3]. Although this approach allows to reach the goal of selectivity, it confers reduced stability to the sensing system which is affected by the fragility of biomolecules easily subject to modifications/denaturation when exposed to not physiological conditions.

Herein, we propose a novel functionalization strategy of nPSi, based on the use of artificial recognition elements instead of natural receptors, conferring it binding abilities toward a model target. In particular, metal-chelating groups are anchored to PSi surface by an easy and simple coupling protocol for possibly exploiting the metal ion mediated interaction with different targets. Specifically, the easy anchoring of copper, iron, nickel and zinc ions is demonstrated by monitoring functionalization steps by X-Ray Photoelectron Spectroscopy (XPS), which allowed to verify also the successful metal removal upon PSi exposure to a strong chelating agent (EDTA) and the metal-ion switching process, enabling to change the bound metal ion with high flexibility thus increasing the versatility of the adopted functionalization protocol. As a proof of concept, the optical detection of the dipeptide carnosine is tested by UV-vis reflectance spectroscopy leveraging the interaction between its histidine moiety and copper ions, mimicking carnosine behavior in natural systems.

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Acknowledgement

This work was partially funded by the European Union Horizon Europe programme under grant agreement No 101046946 (RESORB).

O12-SB

A NANO-PLASMONIC BIOSENSOR FOR FAST AND HIGHLY SENSITIVE DETECTION OF NANOPLASTICS

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Nanoplastics are a global emerging environmental problem. Despite the relevance of the issue, fast, quantitative and reliable *in situ* analytical approaches to determine nanoplastics are not yet readily available. The aim of this work was to devise an optical sensor with the goal of direct detecting and quantifying nanoplastics in seawater.

The biosensor was developed by grafting onto a gold-nanograting (GNG) plasmonic platform[1] a biological receptor[2] as recognition element. As a result, the biosensor required just minute sample volumes (2 µL), allowed rapid detection (3 minutes) and enabled to determine nanoplastics in simulated seawater with a linear dynamic concentrations range across five orders of magnitude (1 - 10000 ng/mL), thus encompassing the expected environmental loads.

At last, the ER-GNG biosensor was tested on real seawater samples and the results were verified by a conventional approach, confirming the ER-GNG sensor offers a straightforward and highly sensitive method for the direct in-field nanoplastics monitoring.

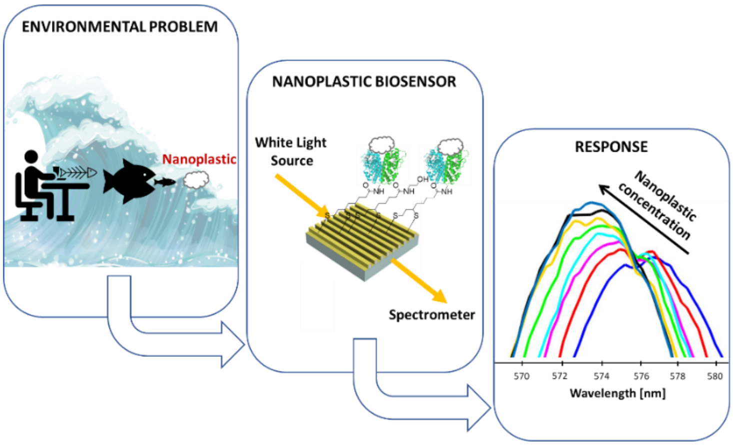

Figure 1: flow chart of the optical biosensor determination of nanoplastics.

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O13-SB

COMBINING NEW LUCIFERASE MUTANTS WITH METAL-ORGANIC-FRAMEWORKS TO DEVELOP NEW BIOSENSING TOOLS

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The availability of new bioluminescent proteins with tuned properties, including stability, emission wavelength and kinetics, is of outmost importance in the bioanalytical field. By tailoring their emission wavelength, blue, green[1], orange, and red emitting luciferase mutants with improved brightness and stability have been obtained with the purpose to improve sensitivity and selectivity of commonly used methods employed for ATP detection and microbial contamination monitoring, among others.
On the other side, different nanomaterials, such as Metal-Organic-Frameworks (MOFs), have emerged as versatile platforms for protein immobilization, offering protection in harsh conditions and enhancing the emission signal of bioluminescence proteins. A new bio-composite, ZIF-8@luc was synthesized and characterized in harsh conditions (e.g. high temperatures, non-native pH, presence of organic solvents), and storage stability, recyclability, precision, and Michaelis-Menten constants (Km) for ATP and D-luciferin was also evaluated. The suitability for ATP detection was also investigated, leading to promising results for ATP sensing also in portable devices, achieving a limit of detection for ATP down to 0.2 fmol[2].
Thus, the combination of bioluminescence and nanotechnologies represents a challenging and promising strategy to obtain new bioluminescent nano sensing systems with the potential to match specific analytical requirements.

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Acknowledgements:

We would like to thank the Ph.D. program on Green topics (PON "Research and Innovation" 2014–2020) funded by FSE REACT-EU.

O14-SB

A DISPOSABLE IMMUNOSENSOR FOR DETECTION OF SALIVARY MMP-8 AS BIOMARKER OF PERIODONTITIS

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Periodontitis is a disease found in the oral cavity which consists of a chronic inflammation of the periodontal tissues, due to the accumulation of dental plaque[1]. Periodontitis starts as a normal gingivitis and can progress onto a chronic and aggressive disease, with periodontal tissue destruction, leading to tooth mobility and tooth loss. Matrix metalloproteinase-8 (MMP-8) was demonstrated to be the most prevalent MMP in diseased periodontal tissue, gingival crevicular fluid (GCF) and saliva, whose concentration correlates with disease severity[2]. Various methods have been reported in literature for quantifying MMP-8 in oral fluids, such as enzyme-linked immunosorbent assay, time-resolved immunofluorescence assay and lateral-flow immunoassays. The only POC devices for salivary detection of MMP-8 available on the market are PerioSafe ® and Implant Safe ® dipstick immunotests, which combine lateral flow technology with ELISA detection.

Voltammetric immunosensors represent interesting alternatives, as they are low cost, fast, easy to use with possibility of POC analysis.

This work describes the development of a novel voltammetric immunosensor for the detection of salivary MMP-8. The electrochemical platform is based on a graphene screen-printed electrode (GPH/SPE) functionalized by gold-nanospheres[3] (AuNSs) and antibodies against MMP-8 protein (anti-MMP-8). The very good performances exhibited by the proposed biosensor allowed its use in real saliva samples, where it showed comparable results to the conventional ELISA method. Therefore, the anti-MMP-8/AuNSs/GPH/SPE based immunosensor may represent a promising tool for non-invasive screening of periodontitis at the POC.

To the best of our knowledge this is the very first time that a voltammetric immunosensor has been developed and applied for MMP-8 detection.

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O15-SB

DIRECT DETECTION OF SINGLE POINT MUTATION BY SUPERPARAMAGNETIC PARTICLES-ENHANCED SPR BIOSENSOR IN LIQUID BIOPSY

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The direct detection of biomarkers in liquid biopsy for early-stage diagnosis and personalized treatment plays a crucial role in controlling the outbreak of disease and increasing the survival rate of patients.[1] Superparamagnetic particles (MPs) have emerged as promising candidates for developing biosensors since they hold highly active surface, great chemical stability, and facility of surface functionalization, which make them excellent magnetic probes for ultrasensitive signal transduction with enhanced sensitivity in real-time measurement by minimizing the matrix effect.[2] Surface plasmon resonance (SPR) is one of the most promising technologies for biomarker detection in liquid biopsy due to its outstanding properties such as rapid and real-time dynamic monitoring.[3]

Here, we propose a MPs-enhanced SPR imaging biosensor to detect single point mutations (SNPs) in nonamplified genomic DNA from both healthy individuals and patients affected by β-thalassemia and colorectal cancer. After the functionalization of MPs (1.0 μm) with biotinylated DNA probe, complementary DNA target sequence has been captured, isolated and, subsequently, discriminated by peptide-nucleic acid probes immobilized onto SPR gold surface. The MP-enhanced SPR assay allows for detecting at attomolar level (2.5 pg μL^{-1}) SNPs of target DNA both in buffer and human plasma with minimal sample manipulation by obtaining reliable results within two hours.

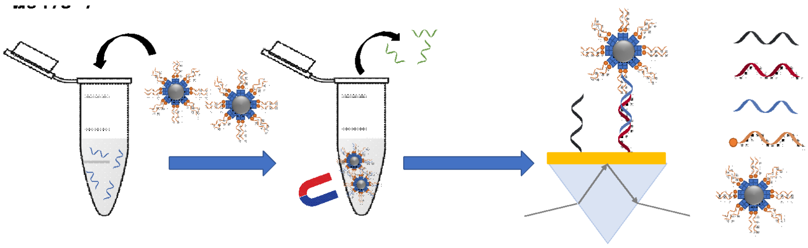

Figure 1: Schematic representation of MP-enhanced SPR assay.

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Acknowledgments to Research and innovation programme 2014-2020 "PON REACT-EU project" and Horizon 2020 ULTRAPLACAD project (grant agreement no. 633937).

HIGH-PERFORMANCE SENSING APPLICATION WITH A STABLE PHYSISORBED ANTIBODIES LAYER

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The phenomenon of antibodies physisorption at a solid interface is a fascinating area of study that holds significant implications for various applications, including the development of biomodified interfaces for biosensor devices[1]. The performance level of those devices can significantly depend on the strategy of biorecognition element immobilization.[1] In particular, the physical adsorption approach is the simplest,[2] being cost-effective, fast, and compatible with printing techniques.[3] Physisorption, despite those huge advantages, is not widely used due to a prevailing belief that it does not result in optimal performance. The lack of uniformity and long-term stability in physisorption have not been studied systematically, particularly in the case of bilayers of capturing antibodies.

Herein, the homogeneity and stability of an antibody's layer against SARS-CoV-2-Spike1 (S1) protein physisorbed onto a gold surface have been investigated by means of a multi-parameter Surface Plasmon Resonance (SPR). The evaluation of figures of merit, such as the limit of detection of 2 nM and the selectivity ratio between the negative control and sensing experiment as low as 0.04, proved the high performance of the sensing. This SPR S1 protein assay is, to the best of our knowledge, highly performing.[4,5] The elicited figures of merit outmatch those measured with more sophisticated biofunctionalization procedures involving the chemical bonding of the capturing antibodies to the gold surface. The present study opens interesting new pathways toward the achievement of a cost-effective and scalable biofunctionalization protocol, which could guarantee prolonged stability of the biolayer and easy handling of the biosensing system.

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O17-SB

MOLECULAR IMPRITED POLYMERS FOR TRACE ANALYSES OF FOOD CONTAMINANTS

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Molecular imprinted polymers (MIPs) are widely used in development of reliable and stable sensors. Indeed, MIPs present a peculiar biomimicking nature respect to different biorecognition elements (antibodies, DNA, enzymes *et simila*), enclosing nanomaterials as nanozymes[1,2]. MIPs are synthesised through a polymerization method to create semi-specific positions for targets in the molecular dimensions by using a monomer (e.g., o-phenylenediamine, pyrrole etc.) and a target molecule[3].

In this work, a MIP based electrode was used to sense 2,4-dichlorophenossiacetic acid (2,4-D) at ultralow/traces concentrations, combining electrochemical techniques (Cyclic Voltammetry, Electrochemical Impedance Spectroscopy) and electronic measurements, carried out using Organic ElectroChemical Transistor (OECT) biosensors. At first, the modified platform was characterized by using different electrochemical techniques to demonstrate the effective removal of the templating molecule and the possibility to perform the rebinding/washing step multiple times, hence proving the stability of the prepared electrode surface. Furthermore, we performed a spectroscopic characterisation of the modified surface by means of X-Ray Photoelectron Spectroscopy (XPS) to prove the efficient template removal. Finally, the platform was also used to perform low-trace sensing measurements using OECT biosensors.

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O18-SB

SYNTHETIC DNA STRANDS CONJUGATED WITH ANTIGENS AND ENZYMES FOR ULTRASENSITIVE ELECTROCHEMICAL ANTIBODIES DETECTION

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Detection of antibodies plays a crucial role in the diagnosis/prognosis of a wide range of human diseases and more recently have gained importance as therapeutic agents for autoimmune diseases and cancer. Due to the low concentration (low nM to pM) at which antibodies are usually found in clinical samples, methods for antibodies detection need to be not only specific and selective but also particularly sensitive. To achieve this goal signal amplification strategies are usually employed, such as in the enzyme-linked immunosorbent assay. This, however, requires reagent-intensive processes and multiple washing and reaction steps that lead to relatively high costs and limit the applicability at the point of care (POC). In response to the urgent need of new analytical tools for the rapid, inexpensive, and quantitative measurement of antibodies, several approaches based on different signaling strategies and that take advantage of the programmability and versatility of synthetic DNA have been recently reported.[1-3] However, all these approaches based on the use of antigen-conjugated DNA strands share a common limitation: due to the direct nature of the assay and the lack of amplification step their sensitivity remains in the nanomolar level. In response to the above considerations, we have developed an electrochemical platform that combines the programmability and versatility of antibody-responsive DNA strand displacement reactions to the sensitivity provided by enzyme amplification to achieve ultrasensitive antibodies detection.[4] We have demonstrated the sensitive (low picomolar detection limit), specific (no signal is observed in the presence of non-specific antibodies), selective (the platform can be employed in complex media, including 90% serum) and multiplexed detection of five different antibodies, including three of which are clinically relevant. For all the above reasons, our platform opens the door for the development of new classes of DNA-based sensors for ultrasensitive detection that may be useful in a wide range of applications, including point-of-care diagnostics.

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O19-SB

DYNAMIC AND REVERSIBLE DECORATION OF DNA-BASED SCAFFOLDS

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Over the past decades many efforts have been dedicated to the use of several biomolecules as building blocks for the fabrication of molecular bio-scaffolds. A positive feature of these structures is that they can be decorated with different ligands and recognition elements to provide a variety of functionalities with potential applications in sensing, bioimaging or drug delivery. Compared to other employed biomolecules, the use of synthetic DNA presents several advantages. The high predictability and programmability of DNA-DNA interactions, together with the sequence-specific addressability of DNA strands allow to achieve the decoration of DNA-based scaffolds at specific locations and with nanoscale precision. Despite this, the methods employed so far are "static" and often lack versatility and programmability. Motivated by the above considerations, we demonstrate here a novel approach to achieve dynamic and reversible decoration of DNA-based scaffolds.[1] To do this, we employ re-engineered DNA tiles containing enzyme-responsive strands covalently conjugated to different molecular labels. These strands are designed to be recognized and degraded by a specific enzyme inducing their spontaneous de-hybridization from the tile and their replacement by a new strand conjugated to a different label. Our approach offers the possibility to control the decoration of higher-order supramolecular assemblies with several functional moieties to achieve functional biomaterials with improved adaptability, precision, and sensing capabilities.

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ELECTROCHEMICAL DETECTION OF DNA THROUGH A VERSATILE MICROFLUIDIC PLATFORM

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Most bioanalytical detection schemes for target DNA fragments necessitate considerable time, effort, and expertise from trained personnel to meticulously conduct the analysis and obtain reliable outcomes[1]. With this in mind, we developed an easily-fabricated microfluidic chip that encompasses all necessary steps for a sandwich-like DNA assay, demanding minimal manual intervention and reduced sample volumes[2].

A suspension containing DNA-modified superparamagnetic microbeads is first introduced into the microchannel of a flow-based chip *via* a peristaltic pump. A magnet ensures their proper positioning. Subsequently, in a continuous-controlled microfluidic flow, the particles are exposed to a series of solutions containing the reagents and the analyte, alternated by washing solutions, following an experimentally-optimized protocol. Post-hybridization, the beads are dislodged from their position and directed into the electrochemical measuring cell. Here, the resulting sandwich-like conjugate can be electrochemically detected at low concentrations harnessing an enzymatic signal amplification reaction.

Efficiency and sensitivity enhancement were achieved by determining the optimal workflow, including washing steps, incubation durations, and individual flow rates for each stage. Consequently, this approach significantly reduced reagent volumes and overall experimental runtime. The system demonstrated its efficacy in the proof-of-concept analysis of short DNA fragments, achieving detection limits in the picomolar range, utilizing only a few microliters of the target DNA sample and presenting results in less than one hour. This platform could be seamlessly applied to the analysis of environmental DNA and DNA collected from clinical specimens, with the promising potential for software-controlled mechanisms to enable complete automatization of the various assay steps. Incorporation of amplification techniques within the microfluidic chip to increase the sensitivity of the platform is also expected.

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Acknowledgements:

Financial support from Regione Toscana Bando Salute 2018 (Research project CUP n. D78D20000870002) is acknowledged.

O21-SB

PAM-ENGINEERED TOEHOLD SWITCH DNA AS ACTIVATORS OF CRISPR-CAS12A FOR SENSING APPLICATIONS

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CRISPR-associated (Cas) nucleases coupled to a single guide RNA (crRNA) are sequence-dependent nucleic acid-targeting systems capable of recognizing and cleaving complementary sequences. The collateral cleavage activity of the CRISPR-Cas Type V system has catalyzed the development of new approaches in the field of *in vitro* diagnostics [1, 2]. Here, we report on the rational design of a PAM-engineered toehold switch DNA hairpin to activate CRISPR-Cas12a collateral cleavage activity in response to a target biomolecule. Using PAM-engineered toehold switch DNA controlled via strand displacement reactions we add programmability to Cas12a-based DNA processing and demonstrate the rapid detection of different classes of analytes as nucleic acids, clinically relevant IgG antibodies, and small molecules. The proposed sensing approach combines in a single-step measurement the signal amplification due to CRISPR-Cas12a multiple turnover collateral cleavage activity with the advantages of target-binding induced DNA hybridization networks.

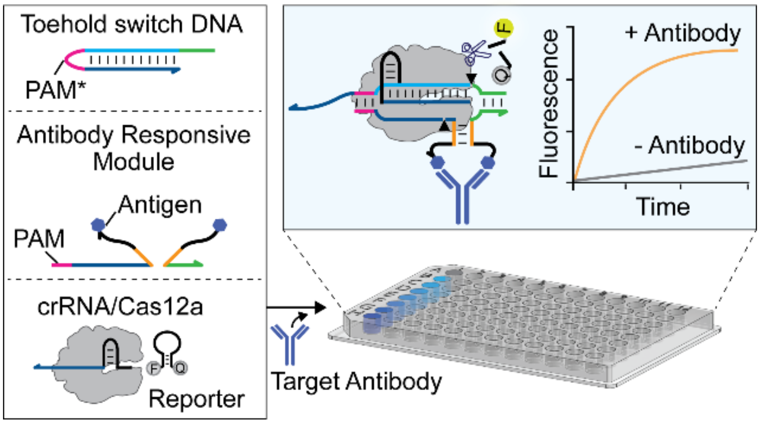

Figure 1: Antibody-induced colocalization of two antigen-conjugated DNA strands induces a conformational change to the DNA hairpin leading to triggering Cas12a collateral nuclease activity.

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Acknowledgments:
This work received funding from the Associazione Italiana per la Ricerca sul Cancro, AIRC (A.P).

O22-SB

Electrochemical aptasensor based on laser-induced graphene electrodes for *Escherichia coli* detection

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The detection and identification of pathogenic microorganisms is of crucial importance as they pose a major threat to worldwide health system as well as an economic burden. In this context, biosensors represent a valuable alternative to classical methodologies due to their intrinsic low-cost, short response time, and portability. In the recent years, the advancements in material science have brought to light a novel, interesting material called, Laser-Induced Graphene (LIG), that has attracted interest due to properties that include: its mechanical resistance, its high surface area, and the relative ease in terms of production processes[1]. These characteristics have opened possibilities to develop low-cost and portable electrochemical devices that can respond to point-of-care applications. In this work, a LIG electrode (Fig. 1A) covalently functionalized with two different aptamers (P12-55 and P12-31[2]) was used for the development of an aptasensor for the detection of *E. coli*. Electrochemical impedance spectroscopy was used to evaluate the change in the charge transfer resistance of the aptasensor upon interaction with the bacterial cells. The aptasensor showed a linear response in the presence of *E. coli* within $10^0 - 10^2$ CFU/mL when tested in phosphate buffer saline solution. Importantly, the biosensor proved to be selective for *E. coli* and negligible response was observed in presence of *Staphylococcus aureus* and *Pseudomonas aeruginosa*. Finally, the sensor was calibrated in urine samples spiked with a known concentration of *E. coli* cells (Fig 1B).

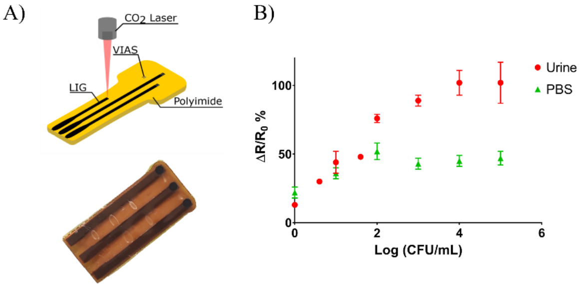

Figure 1: A) LIG electrodes scribed on polyimide. B) Calibration curves at increasing concentration of *E. coli* in phosphate buffer saline and in urine.

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O23-SB

ENTROPY DRIVEN CELL-FREE TRANSCRIPTION SENSORS

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Here we created a new strategy that allows us to rationally control cell-free transcription. To do so, we re-engineered a well-known double-stranded DNA template, giving it structure-switchable properties. In this approach, the polymerase promoter domain is connected by the intrinsically disordered loop. The promoter also contains a nick, which enables template opening and closing, that is guided by the entropy of the loop. By increasing the loop size, the transcriptional activity is decreased, and vice versa (Fig. 1a). To monitor this, the template sequence was designed to generate a light-up RNA aptamer. Furthermore, the loop domain can be redesigned to respond to different molecular inputs, which in turn is followed by an increase in transcription (Fig. 1b). The stimuli-responsive domain can recognize both nucleic acids and small molecules. This engineering approach could potentially enable a simultaneous, controlled production of different RNAs at different rates, upon recognition of different inputs. That could provide a new tool for the development of innovative sensing platforms based on cell-free systems, and expand the range of molecular inputs that allow the metabolic processes control in artificial protocells.

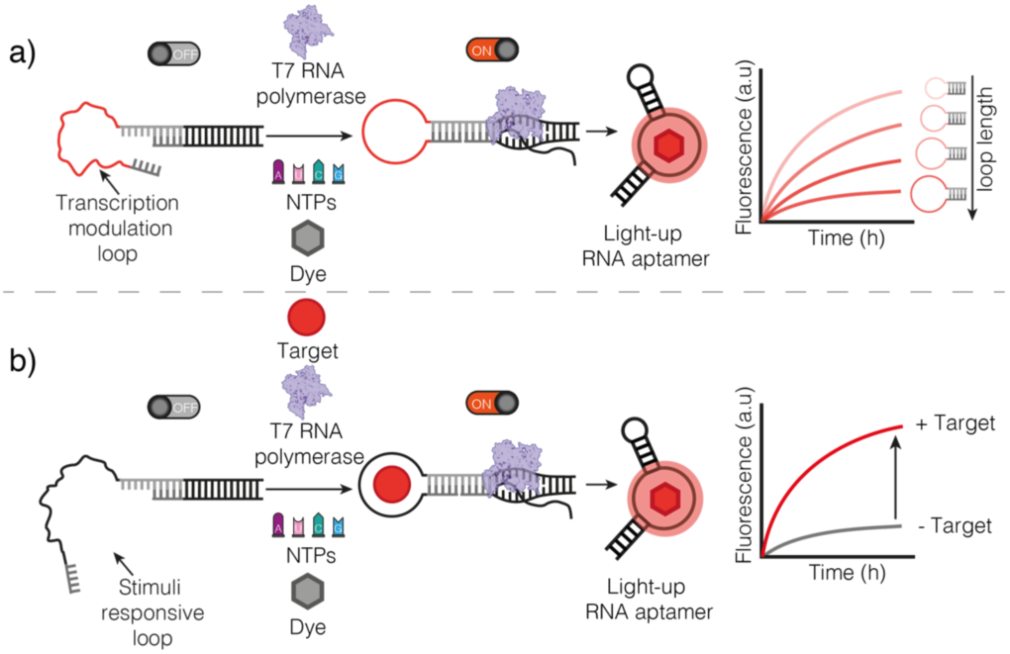

Figure 1: a) Rational control of cell-free transcription is achieved by introducing an intrinsically disordered loop and a nick, that together enable template structure-switching. b) The loop can be redesigned as a stimuli-responsive element, making the transcription activated upon target recognition.

O24-SB

TOWARDS OPTODES FOR ALBUMIN DETECTION: EXPLORING THE COUNTLESS OPPORTUNITIES OF SULFONPHTHALEIN DYES AS RECEPTORS

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Since the first ground-breaking studies on bromocresol green (BCG) colour-changing mechanism upon interaction with bovine and human serum albumin (BSA and HSA),[1] these methods gained a predominant role in laboratory procedures and in commercial assays.[2] Other dyes have been randomly tested,[3,4] but, among all, BSA detection at acidic pH exploiting BCG transition from yellow to blue at increasing protein concentration (Figure 1a) definitely represents the most common method, still in use nowadays.[1]Coming across this "old literature", some questions immediately popped up in our mind: why only BCG? Why not testing other dyes with similar structures? What would happen at different pH values? Aren't we missing something interesting? To answer these questions, we set up a rational investigation of sulfonephthalein dyes reactivity towards BSA, exploiting different pH values (from 3.5 to 9.0, in respect of protein stability) and ionic strength. Besides a full characterisation with different techniques (UV-Vis, CD, ^{1}H-NMR, fluorescence), firstly we identified the most convenient experimental conditions for BSA quantification by Partial Least Square regression run on UV-Vis spectra (Figure 1b). Secondly, we found out several combinations of dyes and operating pH that allow naked-eye detection of BSA and thus could be promising for optodes development.

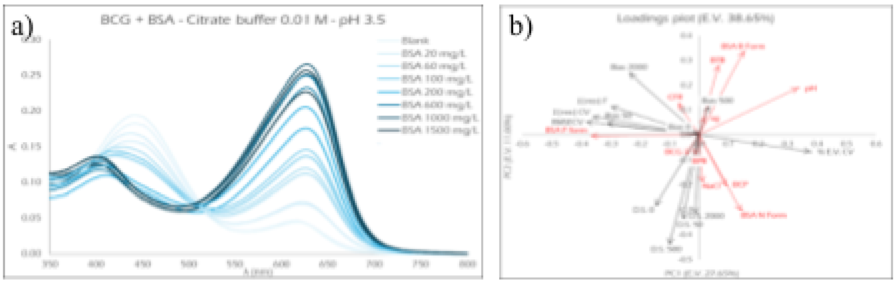

Figure 1: UV-Vis spectra of BCG (10µM) in citrate buffer 0.01 M at pH 3.5 upon addition of BSA (0-1500 mg/L) (a); Loadings plot of PCA run on PLS models' performances, obtained at different operating conditions (b) .

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O25-SB

2D NANOMATERIALS FOR BIOLOGICAL APPLICATIONS

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Early diagnose is a crucial step to improve the patient's expectancy of life and the quality of the treatment. This is particularly true in the case of tumours, where "circulating tumour cells" (CTCs, i.e. tumoral cells that can move through the cardiovascular and the lymphatic systems) elicit the growth of metastases even years after the surgical removal[1]. The identification of CTCs is of great interest for the definition of an early treatment; however, CTCs detection is challenging because of their low concentration (about 1–100 cells/mL) and small size (tens of µm on average)[1]. 2D nanomaterials have been widely studied in the last decades because of their large surface area and peculiar optical, mechanical and electrical properties[2], which make them suitable for improving biosensing performance. Among 2D nanomaterials, Transition Metal Dichalcogenides (TMDCs) and MXenes have gained great attention in the clinical field as highlighted by the constant growing of published papers[2,3]. Our work aims at tuning the electrical properties of semiconducting (WS_2 and MoS_2) and conducting materials ($Ti_3C_2T_x$) for fabricating immuno- field-effect transistors (immunoFETs) capable of detecting CTCs in blood samples. Since the delamination procedure strongly influences the conduction properties of 2D nanomaterials[4,5], we investigated the thickness and structure of the synthesised materials by means of SEM, XPS and XRD techniques. UV-vis spectroscopy was employed to estimate the bandgap of MoS_2 and WS_2 in solution, yielding results comparable to those reported in literature[5,6]. Preliminary tests on cell adhesion to different surfaces (functionalised glass and gold screen printed electrodes) were performed to study the capability of tumoral cells of sticking on artificial surfaces.

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O26-SB

GRAPHENE-BASED SMART INKS FOR ELECTROANALYSIS

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Originally discovered as a black pigment, carbon ink played an essential role in human civilization by helping to transmit and spread knowledge. The recent discovery of nano-structured carbon materials (e.g., fullerenes, carbon nanotubes and graphene) are enabling a new generation of programmable inks able to implement advanced functionalities far beyond color.[1] The coupling of these functional inks with modern printing technologies is revolutionizing the field of flexible electronics, and of wearable and implantable sensors and actuators. This talk will elucidate different strategies, spacing from chemical functionalization to self-assembly and phase engineering, to achieve graphene and 2D material-based inks responsive to chemical concentrations.[2,3] In particular, our efforts have been focused in developing multifunctional inks able to fulfil all the requirements of an electrochemical sensor: immobilization and stabilization of the bioreceptors, recognition of the analyte, transduction, and amplification of the signal.[2,3] These smart inks were used to fully inkjet-print electrochemical paper analytic devices (e-PADS), obtaining low-cost, sustainable, and reliable platforms for electroanalysis.[4]

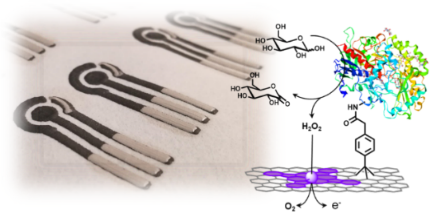

Figure 1: Electrochemical paper-based analytic devices (e-PADs), fully inkjet-printed with graphene-based smart inks.

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O27-SB

Nanomaterial-based Strategies for Enhanced Electrochemiluminescence Biosensing

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ECL is luminescence generated by electrochemical reactions, and for this reason it possesses better spatio-temporal control and low background in comparison with photoluminescence or other optical methods that rely on external light illumination[1]. In the last 20 years ECL has proved to be a versatile and powerful analytical technique, widely used in different fields, ranging from fundamental research to commercial clinical and biological applications[2,3]. ECL is indeed a surface-confined process and a comprehensive control of spatial distribution of the ECL signal at nanometric distances is critically important in view of its applications in sensing devices[4]. Herein I will present some recent strategies in which nanomaterials are used as tool for exploring the mechanism underlying ECL signal generation at nanoscale using luminophore-reporter-modified DNA-based nanoswitches and Dye-doped Silica nanoparticles. By unraveling the intricate processes governing ECL at the nanoscale, these strategies enable the development of highly sensitive and specific biosensors.

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Acknowledgements:
The work is partially supported by the FSE-REACT-EU, PON Ricerca e Innovazione 2014-2020 DM 1062/202, Cod: 19-G-12549-3.

O28-SB

TAILORING ZnO-BASED PIEZOTRONIC SENSORS BY CHEMICAL SPECIATION

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This work shows the potentiality of analytical speciation as a precious tool in the hands of a chemist to design ZnO nanostructures (n-ZnO)[1] and tune the performances of the resulting sensors (Figure 1). This principle was firstly applied to 1D n-ZnO piezotronics wearable heartbeat piezotronic detectors, prepared at mild conditions (85°C, 12 hours) on flexible circuit boards[2] and to the seamless integration of 2D n-ZnO (85°C, 24 hours) onto flexible ITO/PET strain sensors devices[3]. The strain sensors show better performances in comparison to 1D ZnO based devices along with self-cleaning properties triggered by the ZnO photocatalytic effect. These devices are easily wearable and indeed allow for the real time piezoresistive monitoring of finger and elbow bending (Figure 1). The resistance variation upon bending (about 4-fold) outperforms similar devices based on 1D -ZnO. Lastly, the two-fold increase of the zinc ions concentrations and the extension of the reaction time to 60 hours, leads to 3D n-ZnO structures, namely ZnO cauliflowers. These systems show excellent photocatalytic activity and are fully integrable into cellulose acetate films to obtain nanocomposites suitable for regenerative medicine platforms.

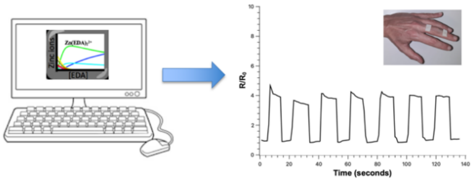

Figure 1. Zinc ions speciation allows the preparation of different analytical sensors each possessing specific outputs. Here, real time finger bending sensor is shown by n-ZnO onto ITO/PET substrates.

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Acknowledgements:
This work has been funded by the European Union-NextGeneration EU─fondi MUR D.M. 737/2021-research project "Zoomer," CUP B79J21038330001 and partially through the MUR-PNRR project SAMOTHRACE (ECS00000022).

O29-SB

EXPLORING THE ELECTROCHEMICAL PROPERTIES OF A NANOASSEMBLY OF CATIONIC CYCLODEXTRIN CARBON NANOTUBES AND FERROCENYL-CARNOSINE

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A nanoassembly based on cationic cyclodextrin carbon nanotubes (CNT-CD) and ferrocenyl-carnosine (FcCAR) was used to improve the electrochemical response of Screen-Printed Carbon Electrodes (SPCEs). The electrochemical response was evaluated by Cyclic Voltammetry (CV) using $[Fe(CN)_6]^{3-}$ as redox probe, whose electron transfer kinetics were affected by the nature of the functional groups contained in the nanoassembly, adsorption processes, and electrostatic interactions between the redox probe and the CNT-CD surface. The electroactivity of FcCAR (Figure 1), even in the presence of heavy metals, was first studied on bare SPCEs[1]. Subsequently, it was investigated on the above-mentioned CNT-CD modified electrodes (SPCE/CNT-CD). The outcomes have already shown the ability of SPCE/CNT-CD to enhance the electroactive properties of the system by up to 84%, especially in the case of Hg^{2+}, and highlighting promising applications for electrochemical detection of heavy metals in aqueous solutions.

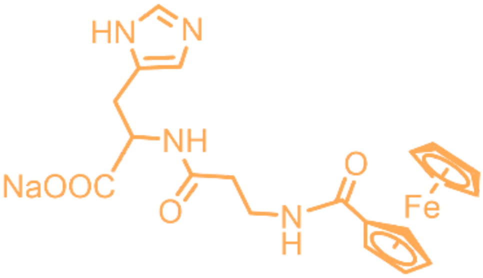

Figure 1: Ferrocenyl-carnosine (FcCAR).

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O30-SB

AuNPs+TiO_2 HYBRID ELECTRODES FOR THE PHOTOELECTROCHEMICAL DETECTION OF CIPROFLOXACIN.

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Nanomaterials have gained extensive use across various fields, including catalysis, energy, and electroanalysis[1], owing to their distinct features such as a large surface area, enhanced selectivity, and favourable surface-to-volume ratio. These materials are highly effective in manufacturing electrochemical sensors capable of detecting contaminants even at low concentrations, including trace levels. To improve the sensors' performances, in terms of detection limits, photo-electrochemical measurements can be employed. This entails utilizing light to generate a stronger electrochemical signal. Various materials, such as semiconductors, can be employed for this purpose. Notably, titanium dioxide (TiO_2) is widely utilized due to its photocatalytic activity[2,3]. However, titanium dioxide does have a few limitations, including fast recombination of photogenerated charges and its reliance on intense UV light for optimal effectiveness. Nonetheless, several techniques can mitigate these drawbacks, including the control of the material's morphology, doping, sensitization through quantum dots, surface cocatalyst deposition, and the creation of heterojunctions[4,5]. Among these approaches, semiconductor-metal nanoparticle heterojunctions have demonstrated significant efficacy[6]. In this presentation, various light sources such as UV lamps and UV LEDs are used in transient photocurrent experiments to quantify ciprofloxacin. The system has been extensively characterized using techniques such as scanning electron microscopy (SEM), atomic force microscopy (AFM), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The combination of a fluorine-doped tin oxide (FTO) glass coated with gold nanoparticles (AuNPs) and a TiO_2 nanoporous film in a hybrid system exhibits superior performance, particularly in terms of sensitivity and lower detection limits, compared to the individual components.

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O31-SB

LABEL-FREE IMMUNOSENSOR FOR THE DETECTION OF PSEUDOMONAS AERUGINOSA IN WATER SAMPLES: STATIC AND DYNAMIC DETECTION

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Pseudomonas Aeruginosa (PA) is the species most frequently associated with disease in humans, where it operates as an opportunistic pathogen capable of causing infections in virtually any organ or tissue. In healthcare settings, water systems may serve as a source of infection for this virus[1]. Considering this, it is evident that effective methods for the prevention and control of these illnesses are required. The research conducted as part of this work stems from the idea of developing a new, accurate and inexpensive label-free electrochemical device capable of determining the presence of this pathogen quickly, reliably and 'in situ'. The peculiarity of the proposed detection system lies in the use of screen-printed electrodes (SPEs) modified with carbonaceous material. This material has the singularity of functioning both as an electrochemical material capable of enhancing the electron transfer kinetics of SPEs and as a substrate for covalent protein binding[2]. To ensure high structural fidelity and performance, an in-depth electrochemical characterization of the immunosensor's layer-by-layer assembly was conducted. The optimized platform was able to detect PA with good reproducibility (RSD% < 10%) and high sensitivity (LOD = 10 CFU/mL). Thus, proving to be a valid device that can be used as a 'warming' system in environments at risk of contagion.

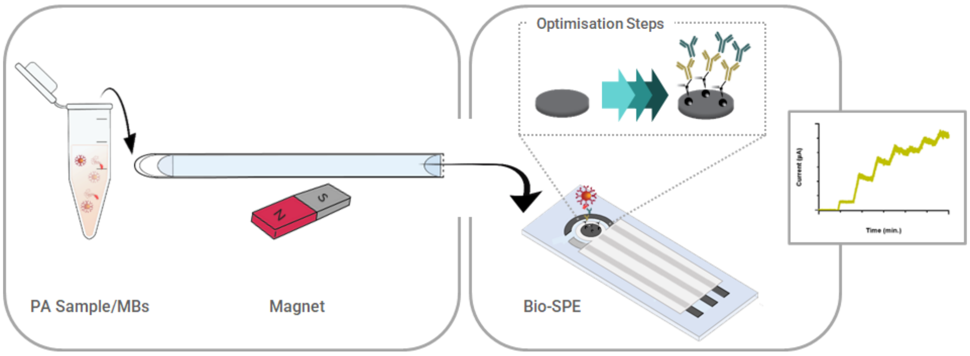

Figure 1. Design of the modified-SPE-based immunosensor for the detection of Pseudomonas Aeruginosa (PA).

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Acknowledgements:
We would like to thank the SANA s.r.l to support this research.

O32-SB

ELECTROCHEMICAL SENSORS FOR FAST DETECTION OF CANNABINOIDS IN *Cannabis sativa* L.

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Two electrochemical sensors are proposed here for the first time for the fast screening of cannabinoids in *Cannabis sativa* L. plant material (inflorescences). The accurate control of the cannabinoid content is an important issue to discriminate among recreational, i.e. illegal, and fibre-type *C. sativa* samples, which differ mainly according to the amount of Δ^9-tetrahydrocannabinol (Δ^9-THC) and Δ^9-tetrahydrocannabinolic acid (Δ^9-THCA).
High-performance liquid chromatography coupled to either UV/Vis or mass spectrometry detection is the preferential technique used for a reliable analysis of cannabinoids in real matrices. However, the non-portable instrumentation, the sample preparation and the analysis time do not allow for their use for *in situ* analysis. As promising alternatives to these techniques, electrochemical sensors have been receiving considerable interest.
In the present study we selected two screen printed electrodes (SPEs), namely a SPE modified by carbon black (SPE-CB)[1,2] and a SPE modified by poly-(3,4-ethylenedioxythiophene) (SPE-PEDOT), to analyse extracts from recreational and fibre-type *C. sativa* inflorescences. The efficiency of the electrochemical procedure in the quantification of Δ^9-THC and of total cannabinoids content has been compared to that of a consolidated method using high performance liquid chromatography, leading to reliable results. Moreover, the sensors' ability to recognize samples containing the various cannabinoids has been explored, coupling voltammetric techniques with chemometric data analysis, suggesting the possibility to discriminate between the different samples of *C. sativa* performing a fast electrochemical measurement.

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POINT-OF-CARE ELECTROCHEMICAL MAGNETOGENOASSAY FOR THE DETECTION OF MUTATED KRAS ONCOGENE

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The need for robust, fast, affordable and portable diagnostic platforms has generated a growing demand for innovative Point-of-care (PoC) diagnostics. Among them, liquid biopsy is used for the detection of several tumour biomarkers, including circulating tumour DNA (ctDNA), in biological fluids[1]. In this context, much attention has been devoted to the detection of ctDNA sequences related to genetic mutations such as those observed in the KRAS oncogene which often occur in early onset of colorectal cancer (CRC). These are single nucleotide polymorphism (SNP) mutations in which a nucleotide is replaced by a different natural nucleotide.

To achieve the detection of SNP-affected ctDNA sequences, we devised a genoassay based on PNA capture probes immobilized on micro-magnetic beads[2]. Two capture probe sequences recognizing wild-type and mutant G12D KRAS ctDNA were used in association with a DNA signalling probe that allows the electrochemical detection using an enzyme conjugate[2]. To achieve maximum differentiation between complementary and non-complementary sequences, the target concentration and incubation temperature were optimized using a 3^2 full-factorial design, obtaining an outstanding specificity given by a remarkably lower (>95%) non-complementary DNA signal compared to that of complementary DNA. Ultra-high sensitivity was achieved in 10-fold diluted human plasma reaching LOD of 818 fM for the G12D capture probe and 1.8 pM for the wild-type capture probe. The genoassay was validated on genomic DNA samples provided by IRCCS-Regina Elena National Cancer Institute, containing wild-type DNA or both wild-type and G12D sequences. The magnetogenoassay was integrated into a smart portable multi-channel potentiostat capable of performing up to four simultaneous acquisitions[3].

The proposed genosensor has proven to be capable of reliably detecting the presence of SNP mutation in ctDNA, useful for personalized medicine applications.

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Oral Scienza-Separazioni

O1-SP

CRYOGENIC MODULATION GC×GC-QqQMS
FOR PESTICIDES DETERMINATION IN HEMP SEED OIL

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The study herein described involves a rapid and limited-volume (0.5 mL) solvent-extraction sample preparation process, without any clean-up or pre-concentration steps, for the determination of 97 pesticides in hemp seed oil.

Hemp seed oil is employed for a wide range of purposes, from cooking to cosmetics, as ingredient in a large variety of body-care and skin products, and in nutritional supplements. It is not only rich in polyunsaturated fatty acids, such as linoleic and α-linolenic acid (in the ranges 50-70% and 15-25%, respectively), but it is also low in saturated fatty acids, with palmitic and stearic acid the predominant ones. In addition, the content of omega-6 and omega-3 fatty acids is characterized by a ratio of 3:1, which is recommended for a healthy human diet. Other important components are tocopherols (vitamin E), which act as natural antioxidants.

Analyses were carried out through cryogenic-modulation comprehensive two-dimensional gas chromatography coupled with triple quadrupole mass spectrometry.

The limits of quantification were in the range 0.01-0.5 mg kg^{-1}. The LoQs were related to the residue limits present in three international regulations (Canada, California, Europe), and were found to be too high in five (Canada) and twelve (Europe) cases.

The accuracy values were in the range between 81.5 and 117.6% with an RSD <11%, while the intra-day and inter-day recovery were in the 10.9-126.7% and 11.2-126.9% range, respectively.

Particular attention was devoted to the evaluation of the matrix effect, which was in the range -97.7-184.0%.

Among the ten samples subjected to analysis, four of them were found to be contaminated, involving seven pesticides, with most over the regulation residue limits.

Acknowledgements:
The authors gratefully acknowledge the Shimadzu Corporation and Merck Life Science for their continuous support.

O2-SP

UNTARGETED PROFILING AND TARGETED DETERMINATION OF CHIRAL LACTONES IN MARSALA WINES USING HEADSPACE SPME FLOW-MODULATED COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY (ENANTIO×POLAR) WITH TIME-OF-FLIGHT MASS SPECTROMETRY

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Among volatile compounds, lactones, particularly γ- and δ-, are important constituents of food and beverage aromas and may be markers of alcoholic beverage aged in wood barrels and aroma adulteration. In such a respect, and considering important aspects related to food authenticity, their determination can provide information on such aging processes. The present research is focused on the targeted determination of fifteen chiral lactones along with the untargeted characterization of the volatile fraction of Marsala wines (a dessert wine), by using headspace solid-phase microextraction coupled to flow-modulated comprehensive two-dimensional gas chromatography (enantio column×polar column) with time-of- flight mass spectrometry and hydrogen as carrier gas. Finally, targeted lactones were quantified by constructing matrix-matched calibration curves, with both limits of detection and instrumental detection limits calculated.

Furthermore, emphasis was devoted to the investigation of Marsala wine volatilome, highlighting the highly complex nature of its headspace, with over 300 compounds tentatively identified.

VACUUM-ASSISTED HEADSPACE-SOLID PHASE MICROEXTRACTION FOR SHORT AND LONG CHAIN FATTY ACIDS IN BIOLOGICAL SAMPLES

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There are variety of studies about dietary fatty acids and trans fatty acids in food source, food intakes and various biological samples such as blood and faces. It appears that high levels of some fatty acids or significant differences in their ratio indicate a variety of diseases (i.e., cancer, diabetes etc.)[1]. Regarding the analysis of fatty acid, attention is required to accurately measure the amount of trans and cis isomers. Even though LC-MS seems to be suitable for separation of long chain fatty acids, the usage of GS-MS is more common due to better sensitivity. Whereas short chain fatty acids and some medium chain fatty acids (up to C10) can be analysed directly, long chain fatty acids (LCFAs) require derivatization. The most common way is esterification to form fatty acid methyl esters (FAMEs). However, analysis of trans fatty acid might be challenging for the incomplete separation of cis and trans FAMEs, poor sensitivity, and double bond isomerization. Head space solid phase microextraction (HS-SPME) is known as a fast and effective method for sample preparation. Some research shows that using vacuum may lead to improve transfer of the analytes from sample to gaseous phase and reach equilibrium or at least increase the signal faster and at lower sorption temperature[3]. In this research, for the first time, a vacuum-assisted HS-SPME (Vac-HS-SPME) GC-MS method was developed for determination of more than 25 fatty acids in faecal and serum samples. Derivatization to FAMEs was applied for LCFA analysis. All the steps of the analysis as extraction, derivatisation, Vac-HS-SPME were investigated to increase the signal and preserve the original concentration and ratio of fatty acid. Design of Experiments (DoE) concept was applied to optimize the analytical method. As an advantage, our vacuum system was not tailored design[3], but we used commercially available tools. By comparing the optimized Vac-HS-SPME and regular HS-SPME procedures we proved that Vac-SPME method was more sensitive, with lower limits of detection (from 0.05 to 10 µg L-1) than regular HS-SPME for almost all target analytes. Intra- and inter-assay precision CVs were ⩽9.0% and ⩽12.5%, respectively. The Vac-HS-SPME method was successfully applied to quantify FAs in samples of 10 healthy subjects.

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O4-SP

A POWERFUL AF4-MULTIDETECTION METHOD FOR CHARACTERIZATION, QUALITY CONTROL AND PURIFICATION OF SELF-ASSEMBLING PROTEINS FROM ENGINEERED E. *COLI* LYSATES

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Protein cages, generated by self-assembling fusion proteins expressed by engineered bacteria, have gained increased interest expanding on possible applications in the fields of vaccine technology and biotechnology[1]. However, the advances in the application field don't match with the lack of efficient analytical strategies able to purify and characterize such systems. Once synthetized by the bacteria, these proteins are purified from the bacterial environment by long multistep protocols before characterization. The latter typically involves expensive, complex, and slow approaches (e.g. TEM, HPLC, SDS-PAGE) which moreover don't always work in native conditions (thus possibly altering the results)[1,2]. We report a method to simply separate, analyse and purify lysates of bacteria engineered to express self-assembly fusion proteins characterized by a SpyCatcher or nanobody domains exploiting an AF4-DAD-MALS-FLD platform. The intrinsic soft separation provided by the AF4 technique combined with the use of a mobile phase (PBS, pH=7.4) mimicking physiological conditions allowed to characterize the systems without any risk of sample alteration. The orthogonal information (MW, size, spectroscopical properties) provided by the platform allowed to identify the fusion proteins, evaluate their aggregation state, estimate their concentration and monitor the evolution of the lysates over time. By analysing lysates differing by engineering procedure or by lysis and post-lysis treatments it was possible to evaluate the impact of each parameter on the lysate content to optimize the biotechnological protocol. Moreover, by collecting fractions of the separated samples, it was possible to obtain purified fractions of the SpyCatcher fusion protein system contemporaneously to their characterization. All these features, combined with the velocity of the analysis (<40min) and the minimal sample requirement (<10uL of lysate) candidate our method as a promising approach to further develop the use such system in modern science.

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O5-SP

QUANTIFICATION OF HEALTH CLAIM-RELEVANT TYROSOL AND 3-HYDROXYTYROSOL IN EXTRA VIRGIN OLIVE OIL AFTER DIRECT HYDROLYSIS

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Extra virgin olive oil (EVOO) is an essential Mediterranean diet component that has become an internationally appreciated food product for its organoleptic characteristics and occurrence of health-promoting compounds, which comprise phenolic alcohols, secoiridoid derivatives, flavonoids, lignans, and phenylpropanoids. The two major secoiridoids occurring in EVOO, oleuropein and ligstroside, are esters formed by compounds characterized by the presence of elenolic acid (EA) in its glycosidic or aglyconic form and either 3-hydroxytyrosol (OH-Tyr) or tyrosol (Tyr). Their occurrence has been associated to the cardioprotective effects of EVOO, evidenced by many scientific investigations. The European Food Safety Authority (EFSA) authorized the claim "*olive oil polyphenols contribute to the protection of blood lipids from oxidative stress*" for EVOO which "*contains at least 5.0 mg hydroxytyrosol and its derivatives (e.g., oleuropein complex and tyrosol) per 20 g of olive oil*". Nevertheless, most producers of high quality EVOO do not take advantage of it because it remains unclear what form the amount of "*hydroxytyrosol and its derivatives*" is to be determined quantitatively. Moreover, the accurate determination of secoiridoids is hampered by several factors, including the chemical instability of these compounds in EVOO that undergo hydrolysis over time, the unavailability of reference standards and the lack of official analytical methods for their exhaustive extraction and quantification.

This communication describes and discusses the results of a study carried out to develop a method for the determination of all free and linked forms derived from secoiridoidic chemical structures of tyrosol and hydroxytyrosol occurring in EVOO[1]. The method is based on the direct acid hydrolysis of the secoiridoid compounds in the olive oil and subsequent separation and quantification of OH-Tyr and Tyr by RP-HPLC with UV detection. The discussion is centered on the optimization of the direct hydrolysis that was optimized using a variety of acids at different concentration, temperature and reaction time, also in combination with a suitable co-solvent. The influence of the considered hydrolytic reagents and reaction conditions is evaluated in terms of the yield of OH-Tyr and Tyr obtained at the different experimental conditions. The thermal stability of OH-Tyr and Tyr originally occurring in the hydrolyzed oil, the validation of the optimized method and a comparison of the results with those obtained by traditional approaches (acid hydrolysis of the extracted polar fraction) are discussed too.

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Acknowledgements:

The research was funded by the European Olive-Net Project (Horizon 2020 European Union funding for research & Innovation) grant number 734899.

POTENTIALITY OF A MIXED-MODE STATIONARY PHASE TO ADDRESS CHALLENGING PEPTIDE PURIFICATION THROUGH PREP-LC

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Peptides are biomolecules with a great potential from the therapeutic point of view, because of their special biological properties. Industrially, the production strategies adopted, such as solid phase peptide synthesis or chemoenzymatic synthesis, produce both the target peptide and a series of impurities. For quality and safety reasons, these undesired species must be removed. Preparative chromatography is the technique of choice for the large-scale purification of biomolecules, and it is generally performed in reversed-phase mode, using traditional hydrophobic adsorbents (e.g., C8 stationary phases). A single separation mode, however, is often unsufficient to reach the purity target imposed by regulatory agencies; therefore, different chromatographic modes are often used consecutively to get rid of several types of impurities[1]. A promising and innovative alternative is represented by mixed-mode columns, which are functionalised with two different ligands on the particle surface, exploiting two retention mechanisms in a single chromatographic step to improve the separation. Especially, when mixed-mode chromatography is used in attractive–repulsive mode, the repulsion performed by the dopant (meaning the ligand having smaller bonding density) on the analytes with the same charge sign pushes them to elute earlier, leading to narrower peaks[2]. This contribution illustrates the comparison of a hydrophobic adsorbent (C8) and a mixed-mode one (C8 + 10% of a charged dopant) for the purification of a crude peptide mixture at preparative scale[3]. Thanks to more-favourable thermodynamics, it was found that, when collecting the whole peak excluding fractions of the peak tail, the mixed-mode column led to an increase in the recovery of roughly +15%, together with a slight improvement in purity at the same time, with respect to the traditional hydrophobic column. In addition, if the whole peak, including the tail, is collected, the performance of the two columns are similar in terms of purity and recovery, but the peptide elutes as a narrower peak with the mixed mode. This leads to a collection pool showing a much-higher peptide concentration and to lower solvent volumes needed, which is a beneficial achievement when targeting more sustainable processes. These results are very advantageous from the industrial viewpoint, because they also involve a decrease in the peptide amount contained in the peak tail, which must be reprocessed again to satisfy purity requirements.

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O7-SP

PIPETTE-TIP µSPE ON CARBON NANOMATERIAL FROM RICE HUSK ASH FOR DETERMINATION OF RESIDUAL FLUOROQUINOLONES IN URINE

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Fluoroquinolones (FQs) are broad-spectrum antimicrobials active against various pathogenic bacteria. Their determination in biological fluids is essential to improve therapeutic efficacy and exclude side effects[1]. The small amount of sample often available in biological analysis creates interest in miniaturized procedures. In this work, a carbon nanomaterial obtained from rice husk ash[2] was used as sorbent for Pipette-Tip micro-Solid-Phase Extraction (PT-µSPE) of FQs in urine, paving the way for disposable extraction units. Preliminary recovery tests were performed in tap water samples (2 mL, pH = 3 formic acid-ammonium formate buffer) spiked with 20 µg/L of 6 FQs, considering the pKa of the analytes and PZC of the carbonaceous material (pH ~ 7). All antibiotics were quantitatively adsorbed showing a good affinity for the material. The best experimental conditions were evaluated in terms of sorbent amount (10 mg and 20 mg) and eluent composition (4 % v/v NH_3-MeOH (85:15); 0.1 % v/v FA-ACN (80:20); 50 mM TBAH-ACN (70:30)), and the eluates were analysed by HPLC-ESI-MS/MS (Multiple Reaction Monitoring mode). The TBAH-ACN mixture was the most promising and, in order to increase the recoveries, the concentration of TBAH and the percent ratio of the two components were further investigated. Recoveries higher than 90 % (*n* = 3) for all analytes were obtained with 10 mM TBAH-ACN (85:15).

The final procedure: 10 mg sorbent phase, 20 strokes adsorption, elution with 2□500 µL □ 10 strokes 10 mM TBAH-ACN (85:15) was then tested on blank urine samples (2 mL, pH = 3 formate buffer) fortified with 20 µg/L of the FQs, followed by a cleaning step (500 µL □ 10 strokes 0.1 % v/v FA-MeOH (95:5)) before the elution. Recoveries ranging from 75 % to 116 % were obtained (*n* = 3, RSD <15 %) for the 6 analytes, evidencing a good extraction efficiency also in the untreated biological matrix. PT-µSPE assays are ongoing in urine at lower concentrations (5 µg/L and 10 µg/L) and the final method will be applied to samples from patients undergoing FQ therapy.

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Acknowledgements:

The authors acknowledge support from the Ministero dell'Università e della Ricerca (MUR) and the University of Pavia through the program 'Dipartimenti di eccellenza 2023 -2027' and the Italian Ministry of University and Research (MUR) and the European Union in the framework of the “PON Ricerca e Innovazione”.

O8-SP

INVESTIGATION ON γ-CYCLODEXTRIN-BASED NANOMATERIALS AS SOLID-PHASE MICROEXTRACTION COATING FOR EFFICIENT EXTRACTION OF HIGH-MOLECULAR WEIGHT POLYCYCLIC AROMATIC HYDROCARBONS FROM ENVIRONMENTAL SAMPLES

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The determination of trace pollutants in environmental matrices is considered one of the most challenging tasks in analytical chemistry, requiring selective and efficient extraction of target analytes. Recently, nanostructured sorbents have emerged as innovative materials owing to enhanced surface area-to-volume ratios, engineered morphologies, and improved preconcentration factors[1,2]. Among these, supramolecular receptors provide unique features in terms of selectivity, being the inclusion of analytes driven by specific interactions and by the host/guest shape complementarity[3].

The aim of this study was the development, characterization and performance evaluation of novel nanocomposite materials based on β- and γ-cyclodextrin-functionalized multi-walled coated nanotubes (β- and γ-CD-MWCNTs) to be used as solid phase microextraction coatings (SPME) for the gas-chromatography mass spectrometry (GC-MS) determination of the 16 EPA-priority pollutant PAHs from environmental samples. Considering their high persistence and low concentration levels in environmental samples[3], attention was paid towards high molecular weight-polycyclic aromatic hydrocarbons (HMW-PAHs). Nanocomposite-based SPME coatings were prepared starting from β- and γ-CD, and COOH-MWCNTs, treated with HNO_3 and H_2O_2 to facilitate the interactions with CDs. The materials were characterized by ζ-potential measurements, thermal analysis, ESEM, FT-IR and X-ray photoemission spectroscopy and compared in terms of extraction performance. The γ-CD-MWCNTs coating provided the highest enrichment capabilities towards HMW-PAHs, up to 3-fold higher compared to the β-CD-MWCNTs, owing to the greater flexibility of the receptor. Quantitation limits below 2.3 ng/L were achieved, lower than those obtained using helical MWCNTs[2]. A deeper investigation on the synergistic role of MWCNTs and CDs in the extraction/complexation was performed in solution by NMR and fluorescence spectroscopy, and in solid state by X-ray diffraction.

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O9-SP

INNOVATIVE THERMALLY ASSISTED ON-LINE SOLID PHASE EXTRACTION-REVERSED PHASE LIQUID CHROMATOGRAPHY APPLIED TO TARGETED NUTRIMETABOLOMICS IN HUMAN BIOFLUIDS

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This study proposes and demonstrates the use of thermal desorption in on-line solid phase extraction coupled with reversed-phase liquid chromatography (on-line SPE-LC) for the desorption of analytes strongly retained by multiple interaction polymeric sorbents[1]. In detail, this analytical strategy was applied to the on-line SPE-LC targeted analysis of a model set of 34 human gut metabolites characterized by heterogeneous physicochemical properties (i.e., octanol–water partition coefficient in the range -0.3 – 3.4). The novel thermally assisted on-line SPE approach was investigated in comparison to conventional room temperature desorption strategies based on the use of (i) an optimized elution gradient or (ii) organic desorption followed by post-cartridge dilution. The thermally assisted desorption strategy has been shown to be better performing and suitable for the development of a reliable and sensitive method for the analysis of the model group of analytes in urine and serum. In more detail, under the optimized experimental conditions, the proposed method provided negligible matrix effects in both biofluids for almost all target analytes. Moreover, method quantification limits were in the ranges 0.026-7.2 µg L^{-1} and 0.033-23 µg L^{-1} for urine and serum, respectively, i.e., comparable to or lower than those reported in methods previously published[2,3].

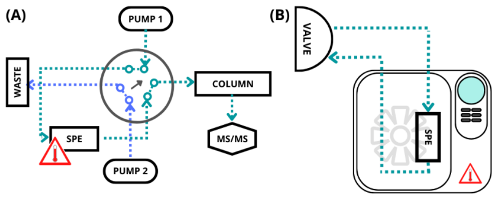

Figure 1: Schematic illustration of the on-line SPE configuration investigated in this study, illustrating (A) the injection phase and (B) the thermally assisted desorption system.

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O10-SP

A NEW HYDROGEL MATERIAL FOR THE ENRICHMENT OF N-LINKED GLYCOPEPTIDES

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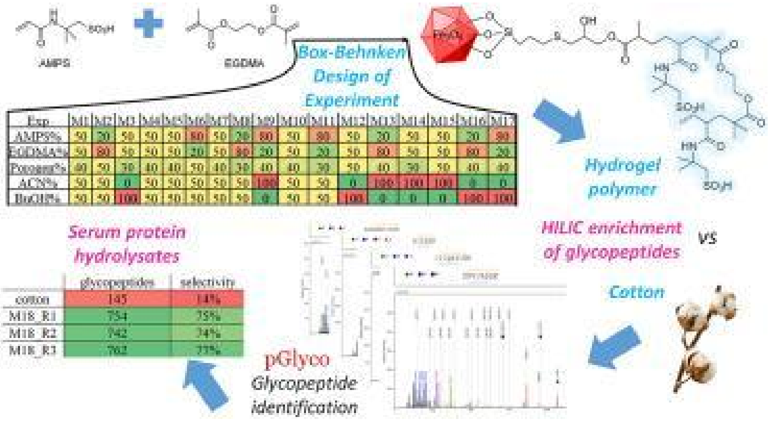
A new HILIC material for the enrichment of N-linked glycopeptides. was prepared using 2-acrylamido-2-methyl-1-propanesulfonic acid as the monomer and ethylene glycol dimethacrylate as the cross-linker[1]. The material was developed by a Box-Behnken experimental design, taking into consideration the amount of monomer-to-crosslinker ratio, the composition, and the amount of porogen mixture. The 17 materials resulting from the Box-Behnken experimental design were employed for the enrichment of glycopeptides from fetuin protein and serum protein digests. The materials displayed a superior performance over cotton HILIC enrichment, both in terms of the number of enriched N-linked glycopeptides and selectivity, providing up to 762 N-linked glycopeptides with 77 % selectivity. The results not only provide one additional HILIC material for the enrichment of glycopeptides but also pave the way for the use and development of hydrogel materials for the enrichment of N-linked glycopeptides.



Exp	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12	M13	M14	M15	M16	M17
AMPS%	50	20	50	50	50	80	50	20	80	50	80	50	20	50	50	20	80
EGDMA%	50	80	50	50	50	20	50	80	20	50	20	50	80	50	50	80	20
Porogen%	40	50	30	40	40	50	40	30	40	40	30	50	40	30	50	40	40
ACN%	50	50	0	50	50	50	50	50	100	50	50	0	100	100	100	0	0
BuOH%	50	50	100	50	50	50	50	50	0	50	50	100	0	0	0	100	100

	glycopeptides	selectivity
cotton	145	14%
M18_R1	754	75%
M18_R2	742	74%
M18_R3	762	77%

Figure 1: Analytical platform developed for the analysis of glycopeptides

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O11-SP

EVALUATION OF THE IMPACT OF PARTICLE GEOMETRY ON THE KINETIC PERFORMANCE OF ZWITTERIONIC TEICOPLANIN-BASED CHIRAL STATIONARY PHASES

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The wide applicability and versatility of macrocyclic antibiotics (like teicoplanin) have fostered their extensive use as chiral selectors in liquid chromatography. Many studies have been proposed about adsorption and interaction mechanisms between enantiomers and teicoplanin selector from a molecular viewpoint[1,2]. However, even if the interaction mechanism is the same on different particle formats (i.e. superficially porous, SPPs, or fully porous, FPPs, particles), kinetic performance may differ. As a matter of fact, it has been experimentally observed that, in some cases, SPPs do not always offer better kinetic performance if compared to FPPs[3]. To shed light on this behaviour, all aspects and characteristics of both SPPs and FPPs need to be carefully taken into account and investigated from a fundamental perspective.

In this work the complete kinetic characterization has been conducted on two zwitterionic-teicoplanin columns packed with 1.9 µm fully- and 2.0 µm superficially-porous particles (FPPs and SPPs) for two racemic analytes: Z-D,L-Methionine and 2-(4-Chloro-phenoxy)-propionic acid. Kinetic studies have been performed through the combination of both stop-flow and dynamic measurements under Hydrophilic Interaction Chromatography (HILIC) conditions.

This study has revealed that, when the analyte is able to fully fit the pocket of the chiral selector, the impact of eddy dispersion and adsorption-desorption kinetics on efficiency is strongly dependent on particle geometry and on the loading of chiral selector.

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O12-SP

FFF-BASED MONITORING OF SURFACE AND STABILITY EVOLUTION OF AIRBORN SUBMICROPLASTICS FOLLOWING ACTIVE TRANSPORT TO BEEHIVES

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The presence of submicroplastics (SMP) in the atmosphere is a new field of research and the available data is still very limited. Honeybees interact with essentially all elements in their environment and bring back pollutants to their hive, where they eventually accumulate and are transferred to pollen, honey, beebread and beeswax. For this reason, the use of honeybees (Apis mellifera) was proposed as bioindicator for the presence of SMPs in the environment[1]. Bee products are vastly marketed as honey, propolis and other derivatives, and pollen has been proposed and commercialized as “super food”. Pollen includes a wide size distribution of micrometric particles, which are also coated themselves with molecular and nanometric substances. This complex system can interact and alter SMP surface promoting or reducing their solubility, stability and ability to be uptaken by biological systems, altering ecotoxicity, and seeping through the pipeline of bee products. The work here proposed aims at exploiting the benefits of a colloidal, flexible methodology to explore the complexity of SMP pollution, focusing on airborn particles. In our study, a set of SMPs of different size, morphology and material, coherent with a real case scenario of sampling from bees, was characterized with and without contact with pollen mixes, using both static measures and the FFF colloidal approach which already proved useful in studying SMP[2]. This combined methodology allowed to profile SMPs and understand fingerprint variations, and to characterize variations in aggregation state, solubility, and eco/biocorona formation.

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O13-SP

IDENTIFICATION OF THE TIANEPTINE TRANSFORMATION PRODUCTS IN RIVER WATER BY UHPLC-MS/MS

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The consumption of illicit drugs is steadily increasing in all parts of the world, especially in high-income Countries. In addition to the tragic social consequences, this phenomenon also has important effects in the environmental field, where drug metabolites or its transformation products (TPs) can be found[1]. For this purpose, it is necessary to develop and validate new analytical methods for their identification and determination in surface water.

In this study, the natural photodegradation of the tricyclic antidepressant tianeptine (TNP) was investigated subjecting ultrapure water solutions of the drug to sunlight irradiation simulated by a solar box system. A new UHPLC-MS/MS method was developed and validated to identify the predominant TPs formed during the irradiation.

The kinetics of TNP photodegradation is the pseudo-first-order (half-life = 12.0 h in ultrapure water). Five TPs were identified in ultrapure water for the first time and the photodegradation pathway of TNP and its mechanism of degradation in water were proposed. Since TNP is currently on sale in some European countries such as France and Spain, but not in Italy, where in 2020 it was included in Table 1 of the Single Text on Narcotic Drugs[2], the presence of possible TNP TPs was investigated by analysing several samples of Nervión river (Bilbao, Spain). The toxicity assessment of the identified TPs was carried out through *in silico* methods.

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O14-SP

IN-DEPTH LC-HRMS ANALYSIS OF THE EFFECTS OF CHLORINE-BASE DRINKING WATER TREATMENTS ON TOXINS PRODUCED BY CYANOBACTERIA

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Cyanotoxins are a complex group of toxins produced by cyanobacteria widely distributed in fresh, brackish and marine waters. Microcystins (MCs), hepatotoxic cyclic heptapetide, are among the most studied and distributed cyanotoxins[1]. For this reason, the World Health Organization published guidelines for drinking-water quality where a threshold for MC-LR was set at 1 µg/L[2]. To guarantee the safety of water supply systems, public water suppliers use different water treatments, including disinfection, to remove harmful biotic contaminants such as cyanobacteria. In Italy, the pre-oxidation of raw surface water is conducted using chlorine-based agents whose efficacy and safety in removing both cyanobacterial cells and cyanotoxins is still debated[3]. In this work, an interdisciplinary study was conducted on cultures of the toxic cyanobacterium *Microcystis aeruginosa*, subjected to different detoxification treatments, i.e. NaClO and ClO_2, at different concentrations and for different exposure times. The study aimed to investigate the effects of these different chlorination treatments to evaluate their efficiency when used at a regulatory level to address the challenges of providing potable water during a severe cyanobacteria bloom event in source waters. Liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS) revealed that microcystins dominated the toxin profile of the investigated *M. aeruginosa* strain and that all treatments may induce cellular damage with a decrease in toxin content in the biomass and an increase of toxins released into the water. Untargeted LC-HRMS screening, also revealed the presence of a novel cyanopeptolin-type peptide, whose tentative structure was hypothesized based on its fragmentation pattern, obtained by LC-HRMS^n (n=1-3) experiments. This new compound was predominantly present in the biomass sample and seem to be affected by all treatments both in water and in biomass samples, giving its oxidized analogue in the treated samples.

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O15-SP

RAPID ANTIMONY SPECIATION ANALYSIS IN NATURAL WATERS VIA FRONTAL CHROMATOGRAPHY-ICP-MS

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Antimony is a naturally occurring toxic metalloid which is considered as a priority interest pollutant. As a matter of fact, limits have been set for its presence in drinking water. Inorganic Sb species include the III and V oxidation states which exhibit different environmental behavior and toxicity, stimulating the expansion of analytical procedures for their speciation, mainly based on the hyphenation of liquid chromatography and spectrometric methods. In this context, we developed a sensitive, high-throughput and cost-effective procedure for the determination of Sb(III) and Sb(V) in water samples by frontal chromatography-ICP-MS (a technique successfully proposed by the authors for As(III)/As(V), Cr(VI) and Methyl-Hg determination[1-3]). The method is based on the separation of the two species by a low-pressure homemade cation-exchange column (avoiding the use of HPLC systems), and the detection of Sb species by ICP-MS (Figure 1). A very short analysis time (3 min) is achieved while keeping detection limits (LODs) below 1 ng/L. The linearity range and possible interferences due to the presence of a large excess of one species over the other were also investigated. Validation was successfully achieved by a spike and recovery strategy on mineral water samples. The procedure is superior to existing ones in terms of analysis time, LOD and ease of instrumental configuration. The extension of the procedure to other environmental matrices (e.g., soils, plants) or plastics (e.g., PET) will be studied by designing a tailored extraction protocol.

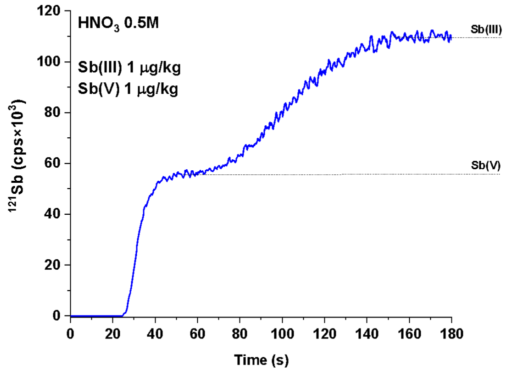

Figure 1: Frontal chromatogram of a 1 µg/kg Sb(V) and Sb(III) solution obtained under optimized conditions.

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Oral Bioanalitica-Omics

O1-B

FPSE-HPLC-PDA ANALYSIS OF ANTIDEPRESSANTS IN BIOLOGICAL MATRICES

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Fabric phase sorptive extraction (FPSE) was applied for the first time to achieve a simple and rapid simultaneous extraction of seven common antidepressant drugs (ADDs) including venlafaxine, citalopram, paroxetine, fluoxetine, sertraline, amitriptyline, and clomipramine in biological matrices. By eliminating the protein precipitation step and reducing solvent consumption, this technique resulted in sample preparation compliant with Green Analytical Chemistry (GAC) principles and avoided the potential loss of analytical information. FPSE, exploiting permeable and flexible substrate chemically coated with a sol–gel organic/inorganic sorbent as an extraction device, specifically based on the sol–gel Carbowax 20 M (sol–gel CW 20 M) coating on cellulose substrate, showed optimal extraction efficiency for ADDs. The drugs were quantified by a well-known and rugged reverse phase high performance liquid chromatography (RP–HPLC) method coupled to photo diode array (PDA) detector. The use of an isocratic elution allows the complete separation of all analytes in only 20 min and simplifies the method transfer to other instrumentations. Chromatographic separation was achieved using ammonium acetate buffer and acetonitrile (AcN) as the organic modifier. The limit of detection (LOD) ranged from 0.04 to 0.06 µg/mL, whereas limit of quantification (LOQ) was 0.1 µg/mL for all analytes except for Venlafaxine, which was 0.2 µg/mL.

Furthermore, real post-mortem samples were analyzed by the herein validated method and the results were then confirmed by the accredited Pharmatoxicology Laboratory (Hospital "Santo Spirito", Pescara, Italy).

O2-B

RESHAPING OF THE MITOCHONDRIAL PHOSPHOLIPIDOME UPON REMOVAL OF FUSION PROTEINS: AN INVESTIGATION BY HILIC-ESI-FTMS

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In recent years, the field of mitochondrial medicine and biology has significantly expanded to encompass diseases associated with issues in maintaining the mitochondrial genome[1], mitochondrial dynamics and quality control[2], and the interaction between mitochondria and the endoplasmic reticulum (ER)[3]. Within this research context, the intricate relationship between the ER and mitochondria has become evident through changes in cellular lipid composition observed when key proteins involved in mitochondrial fusion, such as optic atrophy protein 1 (OPA1) and mitofusins 1 and 2 (Mfn 1 and 2), are deliberately removed by inactivating their respective genes[4]. To gain a deeper understanding of the relationship between these proteins and the mitochondrial lipid profile, a systematic investigation on the phospholipids present in the mitochondria of mouse embryonic fibroblasts (MEF) lacking OPA1 or Mfn 1 and 2 was carried out by HILIC-ESI-FTMS. We successfully identified and quantified more than 160 distinct phospholipids in the mitochondrial lipid extracts obtained from MEF. These phospholipids belong to various classes, including phosphatidyl-cholines (PC, 63), -ethanolamines (PE, 55), -inositols (PI, 21), and cardiolipins (CL, 28). When comparing the OPA1 and Mfn 1/2 knockout samples to the wild-type MEF, we observed a gradual decrease in the presence of alkyl/acyl PC and PE. Furthermore, through the elaboration of LC-MS data by principal components analysis and hierarchical cluster analysis, we detected a general increase in the degree of unsaturation within the side chains of species included in all four phospholipid classes. These findings imply that a subtle reshaping of the mitochondrial phospholipidome occurs in the absence of OPA1 or Mfn 1/2 proteins. Consequently, these observations offer fascinating possibilities for unravelling the mechanisms underlying the significant alterations observed in the mitochondrial ultrastructure when these proteins are lacking.

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O3-B

SUPER SILAC-BASED EPIPROTEOMIC AND LABEL-FREE QUANTITATIVE SWATH-MS ANALYSIS OF PANCREATIC CANCER STEM CELLS

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An advanced approach, combining a label-based super-SILAC MS strategy with a label-free quantitative SWATH-MS analysis, was applied to an *in vitro* cellular model of pancreatic cancer stem cells (PCSCs) for the first time, in order to investigate the profile of histone posttranslational modifications[1] (epiproteome) and the related modulation of proteome during the de-differentiation process. PCSCs are de-differentiated quiescent cells, playing a major role in chemoresistance and metastasis in pancreatic cancer (PDAC), whose de-differentiation depends on epigenetic changes such as histone PTMs. Panc-1, PDAC cells, were used as model and PCSCs were induced by a selective medium. nLC MS/MS analyses of peptide samples, obtained from extracted histones mixed with super-SILAC mix, resulted in quantitative data of histone acetylation and methylation in PCSCs grown for 2, 4, and 8 weeks versus control cells. The heatmap of the log2 of ratios displayed that specific histone marks are dysregulated during the de-differentiation of PCSCs from 2 to 8 weeks of culture. Multivariate (unsupervised PCA and supervised OPLS-DA) combined with univariate (Student's t-test) analyses were performed, finding for example that: H4K20me3 (implicated in quiescence) and H3K9me3 (implicated in chemoresistance) histone marks are induced, together with others, in PCSCs. In addition, dysregulation of intracellular proteins of PCSCs during the de-differentiation was examined using the SWATH-MS approach, which provided accurate and precise quantification of protein abundances and large-scale identification. Among the differentially regulated proteins identified, which can potentially represent therapeutic targets against PDAC, there were some histone methyl-transferases, epigenetic regulators, and enzymes involved in 1C-metabolism that affects histone methylation. In conclusion the application of advanced bioanalytical approaches allows for the first time the in depth description of histone marks and epigenetic-related proteins in PCSCs. This model can be extremely useful in the identification new therapeutical targets, leading to novel therapeutic strategies against PDAC, which usually do not affect PCSCs.

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O4-B

BREATH AND DRIED BLOOD SPOT ANALYSIS COMBINED WITH CARDIOPULMONARY EXERCISE TESTING AND ECHOCARDIOGRAPHY FOR MONITORING HEART FAILURE

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Heart failure (HF) is a complex syndrome that results from a structural or functional impairment of ventricular filling or ejection of blood affecting more than 64 million people worldwide[1]. Cardiopulmonary exercise testing (CPET) combined with echocardiography stress test (ESE) provides a non-invasive evaluation of exercise capacity, ventilatory efficiency, and cardiac function allowing to improve the early diagnosis and the patient management. Nevertheless, clinicians are seeking new approaches to provide a comprehensive metabolic and pathophysiologic picture to further improve the clinical outcome. This work describes for the first time a pilot study that combines breath and dried blood spot analysis with CPET-ESE. Samples were collected before and during exercise using procedures already standardized in our laboratory[2,3]. We prospectively enrolled 43 HF patients together with 54 control patients with cardiovascular risk factors, including hypertension, type II diabetes or chronic ischemic heart disease. Results confirm the central role of breath acetone as an indicator of HF severity since it significantly correlates with NT-proBNP in plasma ($r=0.646$, $p<0.001$). At rest, HF patients showed increased breath levels of acetone and pentane as well as resolvin-d5 and 5-F2t-isoP. At peak effort, breath acetone, PGD_2, PGE_2, and 20-HETE levels in HF patients differed significantly from those of the control group.

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O5-B

INVESTIGATION OF ACYLCARNITINE BIOMARKERS IN PROSTATE CANCER TISSUE BY HIGH-RESOLUTION MASS-SPECTROMETRY AND RETENTION TIME PREDICTION

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Acylcarnitines play important roles in fatty acid oxidation and branched-chain amino acid metabolism, and their disturbance has been associated with the occurrence and development of many diseases[1]. Previous studies have correlated altered levels of acylcarnitine with the progression of prostate cancer (PCa)[2], the most commonly diagnosed cancer in males and one of the leading causes of cancer-related deaths. Currently, the measurement of prostate-specific antigen levels in the blood is affected by limited sensitivity and specificity and cannot discriminate PCa from benign prostatic pathologies. In this regard, untargeted metabolomics represents a powerful strategy for identifying novel and more specific biomarkers[3]. For structurally-related classes of compounds, strategies could be put in place to simultaneously make data analysis more straightforward and achieve more confident identification results. In the present study, the acylcarnitine profile of prostate tissue was investigated. A cohort of 25 PCa patients undergoing radical prostatectomy was collected at the time of the surgical removal. For each patient, samples from both the sane and cancer tissue were collected and analyzed by high-resolution mass spectrometry to obtain a patient-matching control sample for each cancer tissue. Given the homogenous nature of acylcarnitines, an innovative data processing workflow based on Kendrick mass defect filtering was implemented on Compound Discoverer software. Later, an extra layer of validation on the putatively identified compounds was obtained by a retention time prediction model. The obtained data matrix comprising the 71 annotated acylcarnitine was finally analyzed by partial least square–discriminant analysis (PLS-DA) in double cross-validation. The classification results were 93.36 ± 0.05 for the cancer tissue and 92.96 ± 0.05 for the sane tissue, demonstrating the key role of acylcarnitine in the progression of PCa.

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O6-B

ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY FOR SENSITIVE DETECTION OF FOOD ALLERGENS IN COMPLEX, PROCESSED AND NOVEL FOODSTUFFS

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Food allergens are typically proteins that can trigger immune responses in susceptible individuals when they eat a food that is otherwise considered safe. The European Union (EU) has identified and labelled 14 common food allergens. However, as food habits continue to evolve, new allergens are likely to emerge[1]. Mass spectrometry (MS) has proven to be a reliable alternative to outdated antibody-based assays for quantifying multiple allergenic proteins in complex matrices. It offers high sensitivity and selectivity. Nevertheless, the sensitive detection of food allergens is influenced by factors such as food processing, the complexity of food products, and the challenge of detecting cross-contamination, which could pose a serious risk to allergic individuals. This study presents and discusses the use of ultra-high-performance liquid chromatography coupled with tandem mass spectrometry to detect trace amounts of milk (casein and whey protein), soybean, and mustard allergens in various complex and/or heat-processed food products. The method is based on established protocols that involve extraction, trypsin digestion, and purification. These protocols are applicable to different food products such as meat, pasta, ham, and processed cookies. To quantify allergenic proteins, following a bottom-up approach, unique and stable marker peptides are necessary and various MS acquisition protocols, such as multiple reaction monitoring (MRM) and data-dependent analysis (DDA) can be pursued. However, when working with new food sources like microalgae and insects, marker peptides need to be recognized on a case-by-case basis, often through preliminary database searches. *In-silico* digestion of potential allergenic proteins is carried out to select possible guide peptides. These guide peptides are then analysed in complex and processed food samples to identify the most suitable quantifier for further method validation. Here, case studies focusing on both cross-contamination[2] and novel food sources[3,4] will be discussed.

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Acknowledgements:

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O7-B

ELUCIDATION OF ZWITTERIONIC AND POSITIVELY CHARGED METABOLITES IN PROSTATE CANCER BY DEDICATED UNTARGETED METABOLOMICS

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Metabolomics is a fundamental science in omics techniques, which allows for providing qualitative and quantitative data on important metabolites involved in human health. Global analysis with a wide metabolite scope is fundamental; nonetheless, sometimes it may fail to focus on important analytes due to unselective sample preparation protocols, which may result in overlooking important information. As such, this issue was addressed for charged and zwitterionic compounds, which due to their chemical properties are challenging to characterize in global studies and need dedicated sample preparation strategies. The issue was studied within the framework of prostate cancer research, where there is an urgency to discover biomarkers alternative to prostate-specific antigen, as it cannot discriminate patients with benign prostatic hyperplasia from clinically significant forms of prostatic cancer. An analytical workflow was developed for the analysis of polar and charged compounds in urine samples, as this class is usually neglected but potentially interesting in cancer biomarker discovery. The use of graphitized carbon black solid phase extraction enabled the purification of these analytes with 10-40-fold analyte enrichment compared to the common “dilute and shoot” strategy. The chromatographic separation was achieved by HILIC chromatography, while the coupling with high-resolution MS/MS analysis using an untargeted method was chosen to maximize the annotation of the expressed metabolites. The detailed analysis of compound distribution among the 32 benign prostatic hyperplasia and 41 prostatic cancer urine samples indicated that 12 compounds were differently expressed and belonged to the classes of carnitine and amino acid derivatives, which were significantly increased in the prostate cancer urine samples.

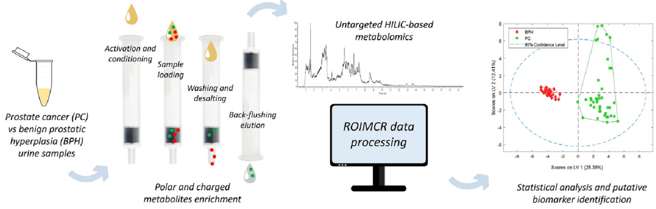

Figure 1: Analytical workflow for polar and charged metabolite investigation in urine sample.

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O8-B

THERMAL STAMPING OF LASER-REDUCED GRAPHENE OXIDE FOR DIRECT ELECTRON TRANSFER-TYPE BIOSENSORS

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Direct electron transfer (DET) of dehydrogenase enzymes has attracted increasing attention in pure and applied bioelectrochemistry over the last decades. One of the most fascinating features of some dehydrogenases is their ability to interact with rationally nanostructured surfaces, resulting in the boosting of DET-event, without the needing for mediators, spacers, and cross-linkers. In this presentation, the DET-ability of Fructose Dehydrogenase (FDH) has been studied toward photo-reduced graphene oxide (rGO) transferred with a new smart approach onto different flexible supports. In detail, graphene oxide (GO) has been photo-reduced with a CO_2 laser plotter, obtaining rGO transferable conductive nanostructured films. The rGO films were transferred onto three flexible substrates i.e. PET-EVA, PET, and PVC, by a here proposed "roll-to-roll thermal stamping" strategy, taking advantage of a simple office-grade thermal laminator. Initially, the electrochemical performances of the rGO-based surface have been deeply studied, and then, their ability to give DET with FDH has been carefully investigated using different concentrations of enzyme. To this aim, dose-response curves of FDH-rGO electrodes have been investigated in the presence of increasing amounts of FRU, ranging from 1 μM to 60 mM, via amperometry (+0.25 V). All the electrodes resulted able to give DET significantly superior to commercial transducers; the most fascinating finding was that, using lower enzyme amounts, the biocatalytic event resulted significantly boosted. The most performing DET-type biosensor was obtained by transferring rGO on PET, further modified with 15 mU of FDH; this biosensor returned excellent sensitivity (LOD = 0.25 μM) and reproducibility (RSD ≤ 4%, n= 3) for the fructose bioanalysis. Noteworthly, the used enzyme units are singifincantly lower (20-time less) compared to the commonly used in literature, while the obtained perfomances resulted superior to the majority of FDH-biosensors. Finally, the rGO-PET biosensor was tested to monitor the fructose evolution in bananas (*Musa acuminata)* during post-harvest ripening; satisfactory recoveries were achieved (109.5-90.3%, RSD < 7%, n= 3), and the selectivity was proved against several potential interfering species. Summing up, this work demonstrates how laser-obtained rGO can be transferred onto flexible substrates using a simple office machine, allowing to construct DET-type biosensors with unique and fascinating features.

Acknowledgements:
This research was funded by the European Union – Next Generation EU. Project Code: ECS00000041; Project CUP: C43C22000380007; Project Title: Innovation, digitalization and sustainability for the diffused economy in Central Italy – VITALIT

O9-B

MONITORING OF THE IMMUNE RESPONSE TO SARS-COV-2 AFTER VACCINATION AND RECOVERY BY LATERAL FLOW IMMUNOASSAY

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The vaccination plans for COVID-19 was undoubtedly the best strategy to return to economical ad social normalcy[1]. Some limitations (supplying of the vaccine dosages or ingredients, organization problems) cause consistent delays to the reaching of the immunization of the population. In addition, the appearance of more contagious variants of the virus implies the need to increase the ratio of vaccinated/not vaccinated population to limit diffusion and guarantee the full protection. Therefore, monitoring the efficacy of vaccination and follow the immune response of vaccinated and/or recovered people is very important to not nullify the efforts made in the vaccination campaigns. Highly accurate laboratory techniques cannot manage such large number of involved samples. Otherwise, antibody detecting point-of-care (POC) testing can fulfil this need. The lateral flow immunoassay (LFIA) is a widely employed POC test for COVID19 diagnosis, and in serological format for antibody detection[2]. A typical serological LFIA includes capture immunoreagents anchored in delimited reactive lines (T and C) and a labelled detectable reagent. The serum is collected in the sample well, flows by capillarity through the strip reacting with T and C. Generally diagnostic tests are developed to increase indiscriminately the sensitivity. Nevertheless, to follow up the immune response progression in time, more than a sensitive qualitative test, a quantitative correlation with the reference serological laboratory method (ELISA) should be preferred. In this work we developed three multitarget serological LFIA devices to detect antibody against the Spike protein (S) and the Nucleocapsid protein (N) from SARS-CoV2 to discriminate the immune response given by recovery from infection and the one promoted by the vaccination. The devices were tested with human sera dosed by reference ELISA, and the color intensity of the test lines was quantitatively acquired. Correlation was used as a figure of merit to define the best strategy for the follow up of the antibody response. The LFIAs for SARS-CoV2 antibody detection include capture antigens, recombinant Spike (S) and Nucleocapsid (N) proteins, and detection reagents, labelled with ruby red gold nanoparticles, different in the three formats (S and N antigens in LFIA-1, protein A in LFIA-2, anti-human IgG antibody in LFIA-3). The LFIA-1 showed the highest correlation with reference ELISA, while the LFIA-2 resulted as the most sensitive. The LFIA-2 was then employed through two strategies (LFIA-2a and LFIA2b) in another format including more test lines to obtain a differently encoded result on respect to the level of immune response, without the need of the signal measurement involving a reader.

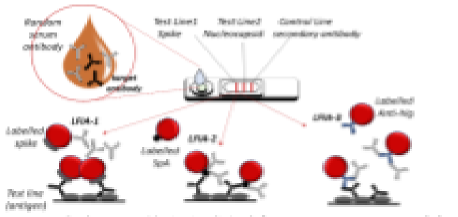

*Figure SEQ Figure * ARABIC 1: Schematic representation of the three formats of serological LFIA for antibody detection of SARS-CoV-2 immune response and correlation with reference serological ELISA method.*

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O10-B

A MULTI-OMICS INVESTIGATION ON BIOLUMINESCENCE IN DEEP SEA FISHES

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Bioluminescence is a prevalent feature in deep-sea ecosystems, with over 75% of species inhabiting the mesopelagic depths (200-to-1000-meter depth range) possessing this capability[1]. Bioluminescent species are found in most of the major marine phyla from bacteria to fish. Bioluminescence plays diverse roles in intra- and inter-specific interactions and has been employed for detecting biological activities and assessing biomass in oceanographic studies. A recently published study has inferred that bioluminescence has evolved independently at least 27 times among 14 major fish clades[2] but despite its widespread occurrence, the mechanistic details and biological pathways underlying bioluminescence in deep-sea organisms are still largely unknown. In this study, we focused on investigating the role of microbiota residing in the light-producing organs of two mesopelagic fish species, *Argyropelecus hemigymnus* and *Maurolicus muelleri*, belonging to the *Sternoptychidae* family. To unravel the mysteries surrounding bioluminescence mechanisms in the dark ocean, we employed a multi-omics approach, including 16S rDNA metabarcoding, metagenomics, metabolomics, and proteomics. Additionally, microscopy-based techniques were utilized to assess the taxonomic and functional characteristics of the microbiome in organs and tissues, including photophores. Through 16S rDNA metabarcoding and metagenomics, we identified specific microbial taxa enriched in the light-producing organs and genes (i.e. LUX A) encoding proteins related to bioluminescence reaction, suggesting their potential involvement in the bioluminescent process. Furthermore, metabolomic and metaproteomic analyses provided insights into the biochemical pathways and proteins associated with bioluminescence mechanisms of prokaryotes and eukaryotes. We detected metabolites and proteins related to LUX A – E pathway including ATP production. The integration of multi-omics data shed light on the potential interplay between the fish host and its associated microbiota in the bioluminescent process. This study significantly contributes to our understanding of the bioluminescent mechanisms in mesopelagic fish species and opens new avenues for exploring symbiotic relationships and evolutionary adaptations between fish hosts and their microbiota in deep-sea ecosystems.

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O10-B

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O11-B

DESIGN OF EXPERIMENT AND UNTARGETED ANALYSIS: AN APPLICATION TO MONITORING EMERGING CONTAMINANTS IN CLAIMS

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Hundreds of new chemicals are produced and released in the environment every year. Many of these, defined as emerging contaminants (EC), may be potentially harmful even at low concentrations, for humans, animals, and the environment itself. The monitoring of EC in different matrices is crucial to unearth contaminated areas or compartments and to evaluate bioaccumulation and biomagnification in the biota. Further, the assessment of exposure levels is important to evaluate the associate risk.

In this light, bivalves are considered good bioindicators to evaluate environmental contaminations, as these animals exclusively feeding by filtering high volumes of sea water. Together with nutrients, they potentially accumulate contaminants present in the water and in the soil where living and, consequently the determination of contaminants in bivalve tissues is representative of the environmental contamination itself.

From an analytical point of view, the characterization and quantification of emerging contaminants in animal tissues is doubly challenging, as analytes are unknow and the matrix is complex. The non-targeted analytical workflow is generally based on ultrahigh performance liquid chromatography coupled to high resolution mass spectrometry (UHPLC-HRMS). In this light, together with the optimization of the instrumental parameters to acquire as much information as possible from samples, it is also crucial the optimization and validation of a general and simple extraction procedure to cover the widest possible range of analytes in term of chemical properties (i.e. molecular weight and polarity). Dispersive solid phase extraction, based on QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) approach, is usually a good compromise, but several parameters should be evaluated.

In the present work, the optimization and validation via DoE of a general extraction procedure based on QuEChERS was proposed for untargeted ECs analysis. The preliminary evaluation was focused on a wide panel of selected contaminants, chosen considering their chemical properties and the EU Watch List. Four method variables (matrix to solvent ratio, percentage of acid in the solvent, salting-out buffer composition and adsorbent for clean-up) at three levels each, were evaluated by a d-Optimal Design approach to optimize the number of experiments to be performed. Analyte responses to modifications of different method parameters were analysed by the CAT software to highlight the best set of values to maximize analyte recoveries.

The optimized and validated method was then applied to the monitoring of a wider panel of known and unknown emerging contaminants in claims sampled in different area of the Venice Lagoon.

O12-B

Kelvin Probe Force Microscopy: a quantitative, label-free and highly sensitive tool for antigen/antibody recognition process

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Kelvin probe Force microscopy (KPFM) is a non-invasive tool for the analysis of changes in sample electrostatic property distributions by measuring contact potential difference between the probe and sample surface. It allows the simultaneous high-resolution topographic imaging of the sample surface, as well as electrical and electronic characterization. In this study, KPFM has been suitably adopted to investigate molecular interactions that lack topological differences but have distinguishable properties in surface potential[1]. The capability of discriminating the changes in surface potential before and after bioassay allows the use of KPFM for developing a diagnostic platform for antigen/antibody immune-complex formation with a sensitivity down to few bindings.[2]

The sensing platform has been demonstrated to be a reliable and label-free on-off device.

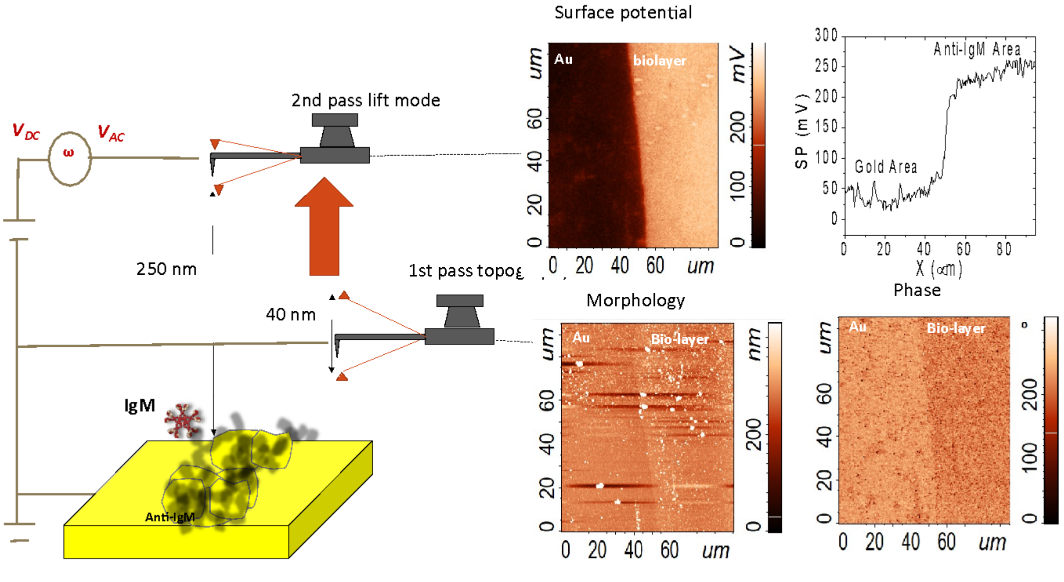

Figure 1: Kelvin Probe Force Microscopy quantitative analysis for antigen/antibody recognition process.

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O13-B

CELECTOR, AN INNOVATIVE INSTRUMENTATION FOR LABEL-FREE SORTING AND QUALITY CONTROL OF LIVING CELLS FOR IMPROVED THERAPY MEDICINAL PRODUCTS

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In the last decade, cell-based platforms have been studied for many innovative applications comprising advance therapy medicinal products (ATMPs), disease models, and effective drug screening through individual customized in vitro drug testing.

To deliver robust and efficient cell-based applications, methods and technologies for cell separation, sorting, or enrichment are required[1]. Stem cells can be found in every tissue, but access is not always easy and cannot be derived in high numbers. Adipose tissue is a very interesting source of mesenchymal stem cells and its use span from aesthetic medicine, for facial and body rejuvenation, to orthopaedic treatments[2].

In this work we present a new automated instrumentation, Celector® (Stem Sel srl, Bologna) for tag-less cell sorting and quality control, using a micro-camera for cell detection and a specifically designed software for image acquisition, post-processing and data analysis. The output of the instrument is a multiparametric fractogram representing number, size and shape of the eluted cells as a function of fractionation time and it is the fingerprint of the cell sample. In this work, we investigated the ability of the new technology to identify and sort sub-populations of the heterogenous expanded adipose derived stem cells, for improved cell therapies.

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O14-B

FFF MULTIDETECTION FOR SIZE-RESOLVED MEASUREMENTS OF DRUG RELEASE FROM PROTEIN-CONJUGATED GOLD NANOPARTICLES

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The conjugates of gold nanoparticles (AuNPs) and proteins are promising systems for drug delivery. Because of its bioaccumulation, targeting, biocompatibility, and surface properties, albumin can transport diverse therapeutic systems in a localized way, which is denoted "spatially controlled release". The interesting optical properties of AuNPs allow them to be monitored using imaging tools, and the photothermal effect can release adsorbed molecules on the AuNP surface, thereby temporally controlling drug release.[1]
Curcumin (Cur) is a polyphenolic compound extracted from the rhizomes of *Curcuma longa*. It is particularly attractive for its antioxidant, antimicrobial, anti-inflammatory, and anticancer effects.[2] This study presents the first application of Asymmetric flow field-flow fractionation (AF4) with on-line UV/vis and multi-angle light scattering (MALS) detection[3] to quantify release profiles of Cur from AuNP-BSA conjugates.
AF4 allows in situ removal of unincorporated drug, while online UV detection selectively provides information on drug binding and release. The method monitors the pH dependence of drug loading and release over time, and the stability of the AuNP-BSA conjugates before and after curcumin loading. Online MALS and offline DLS allow to monitor the size changes of AuNP-BSA-Cur upon drug release.
Overall, with the support of a dialysis model and AF4, we were able to evaluate the Au-BSA-Cur drug carrier from synthesis to the release stage, while the use of multi-detection enabled us to accurately monitor the changes in each stage.

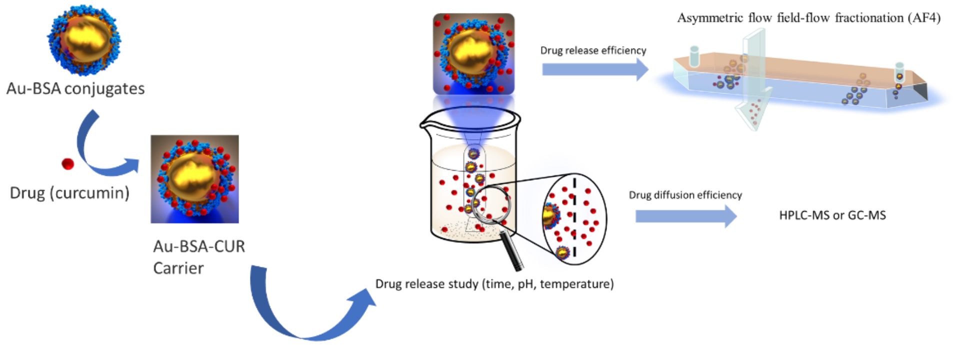

Figure 1: Synthesis of the Au-BSA-CUR drug delivery system and drug release study based on AF4 technology.

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O15-B

CRISPR-CAS-ASSISTED AMPLIFICATION FOR IMPROVED MMP2 PROTEASE DETECTION VIA PEPTIDE-PNA TRANSLATOR

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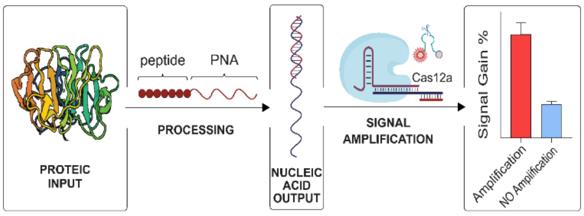
DNA nanotechnology offers unparalleled possibilities for establishing artificial communication among biomolecular species based on programmable nucleic acid interactions. Furthermore, CRISPR-Cas-based technologies are revolutionizing molecular diagnostics by enabling novel signal amplification strategies. Building upon this potential, our study presents a novel sensing platform that specifically targets the protease MMP2, a biomarker associated with various types of cancer.[1] We have developed a chemical translator comprising two different functional units – a peptide and a peptide nucleic acid (PNA) – fused together. The peptide unit incorporates the consensus sequence essential for detecting the target protease, while the PNA unit enables the conversion of the protein-based input, i.e., peptide cleavage, into a nucleic acid output, which can be subsequently amplified. After assessing the translator's efficient proteolytic cleavage by MMP2, we have immobilized it on micrometric magnetic beads as material supports, and we have determined the cleavage kinetics and the specificity of the platform for the selected protease. We then introduced a rationally designed single stranded DNA anchored to the PNA sequence of the translator. This ssDNA carries a tail that is complementary to the Cas12a-bound RNA. Upon hybridization, the nuclease trans-cleavage activity of Cas12a is constitutionally activated, leading to the degradation of FRET-labeled DNA reporters.[2] Consequently, an amplified fluorescence signal is generated. Through this strategy, we were able to successfully detect MMP2 in the low picomolar range based on its enzymatic activity, achieving a limit of detection orders of magnitude lower than that of commercial peptide-based kits. Beyond its immediate implications, our study establishes crucial molecular design principles that can expand the applicability of this approach to diverse proteases. This platform holds promising potential for the detection of biomarker proteases in cell cultures and in tissue samples.



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Oral Forense, Tossicologia e Salute

O1-FT

MULTIVARIATE MODELLING IN HAIR TESTING – MODELLING THE HAIR COLOR BIAS AGAINST DISCRIMINATION

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The main objective of hair testing is ideally to deduce the exposure of the tested subject to a certain substance from its concentration detected in his hair. In practice, this objective is far from being achievable, because the correspondence between exposure and the detected hair concentration depends on a multiplicity of uncontrolled factors of various origin. Some of these factors introduce inconsistency between “real” and “detected” hair concentration and involve matrix variability (color, thickness, aging) and methodological faults (incomplete extraction, inaccuracy). Further unpredictability relies on personal factors, including genetic, physio-pathological, and behavioral differences.

Despite these uncertainties, hair testing proved to provide valuable results, possibly because, in the majority of the investigated cases, most of these factors have little effect or statistically compensate one another. However, the final results run into an increasing risk of being challenged. Multivariate modelling represents a helpful tool to rationalize some of these factors, including the statistical correlation between “exposure” and “detected concentration”.

The following illustrative question is proposed: is it possible to predict for a certain (possibly new) substance how much its incorporation depends on the hair color, without making any dedicated experiment? The tentative answer is yes, as long as we can build a statistical model that connects the hair color discrimination factor with a reasonable number of molecular features, describing the physical and chemical properties of the investigated molecule. An experimental method is proposed for building such a model: (i) grizzled hair are collected from a large number of individuals; (ii) for each individual white and dark hair are treated separately and analyzed by a wide multi-targeted method for prescription and abused drugs; (iii) the concentration differences for the detected substances are annotated with reference to their molecular structure; (iv) the dependence of these differences on over one-thousand molecular descriptors is checked by means of different machine learning algorithms combined with several features selection strategies.

O2-FT

METHOD FOR DIRECT ENANTIOMER DETERMINATION OF METHORPHAN IN SEIZED DRUGS AND BIOLOGICAL SPECIMENS BY MEANS OF CHIRAL HPLC-MS/MS

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Methorphan is a morphinan derivative whose enantiomers show distinct pharmacological and toxicological effects. The levorotatory isomer, levomethorphan, is a strong analgesic drug strictly controlled as narcotic. On the other hand, the dextrorotatory isomer, dextromethorphan, is an antitussive drug, available in many over-the-counter cough suppressant formulations, which does not produce any analgesic effect at the therapeutic dose. However, at higher doses it is responsible for hallucinogenic and dissociative effects, which can be fatal.

In this study, an LC-MS/MS method was developed to determine methorphan enantiomers in heroin seized drugs described as high-potency heroin (HPH), as well as in biological specimens collected from intoxicated people (urine and blood).

Analytical standards of the two enantiomers were used for method optimization, starting from the LC separation, which was achieved on a vancomycin-based column (Astec Chirobiotic V, 250 mm L x 4.6 mm i.d. x 5 μm d.p.). Separation was obtained within less than 15 min, with enantioselectivity (α) > 1.2. Multiple reaction monitoring transitions were used for identification and quantitation purposes. Calibration curves were built in the 0.001 – 5 ppm range by the external and internal (nalorphine) standard methods. After proper validation, the method was applied for the analysis of seized drug powders and biological samples.

Results showed that seized powders contained dextromethorphan in highly variable amounts, ranging from 3 to 1000 ppm. Levomethorphan was found only in one seized powder at a concentration around 0.2 ppm. Dextromethorphan was determined in the biological specimens in the 1 ppb – 1 ppm range.

O3-FT

STUDY OF METABOLOMIC PROFILE ALTERATIONS INDUCED BY OPIOIDS IN MURINE MODELS BY UHPLC-HRMS.

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The proliferation of NPS and the challenges associated with their detection drove forensic toxicologists to identify suitable analytical strategies for their identification[1]. Untargeted metabolomics has demonstrated to be a promising approach for the detection of endogenous markers of NPS assumption[2]. In this study, this tool was exploited for the identification of biomarkers that may indicate the probable intake of opioids of different chemical classes - by exploiting an in-vivo study in mice and HPLC-HRMS analyses. Urine samples were collected from CD-1 mice, both males (n=8) and females (n=8). All animals were initially treated with 0.9 M NaCl-containing saline (vehicle) by intraperitoneal injection; urine was collected cumulatively over 24h. Subsequently, half of the animals of both sex were treated with 30 mg/kg morphine while 6 mg/kg fentanyl was administered to the rest of the animals; then 24h urine was also collected. Samples were diluted prior to UHPLC-HRMS analysis. Mass spectra were acquired on an Orbitrap Q-Exactive mass spectrometer equipped with a HESI source; every sample was analyzed with both RP and HILIC chromatography in both polarities. Multivariate statistical analysis was carried out on the metabolomic data. The OPLS-DA results (the number of variables was reduced until the best Q^2 value through the application of successive OPLS-DA models), led us to identify the main differences in terms of metabolites after drug administration; for example, 5-aminovaleric acid and creatine and others belonging to the main lipid oxidation and amino acids degradation pathways, were among the most altered metabolites. Subsequently, the peak areas for each compound in the vehicle group was subtracted from the peak areas for the compound in the same mouse after drug administration, using each mouse as its own control. Similarly, a multivariate analysis was performed to elucidate differences related to the sex of the animals. The present study investigated alterations in metabolic pathways of CD-1 mice treated with opiates, highlighting the potential of metabolomics in forensic toxicology for investigations related to NPS.

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O4-FT

DEVELOPMENT OF A NEW LIQUID PHASE MICROEXTRACTION METHOD FOR THE DETERMINATION OF SEVERAL ILLICIT DRUGS AND NPS IN ORAL FLUID BY HPLC-MS/MS ANALYSIS

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Over the past decade, there has been a diversification of the substances available on the drug markets. In addition to traditional plant-based substances – cannabis, cocaine and heroin – the past decade has shown the expansion of a dynamic market both for new synthetic psycoative drugs and the non-medical use of pharmaceutical drugs or even prescription medicines. The availability of more potent drugs, the increasing number of substances and their consecutive or sequential use among occasional or regular users, poses a great challenge to the prevention of drug use and the treatment of drug use disorders[1]. For these reasons, innovative methodologies to isolate and identify these molecules are of great interest. The aim of this work was the development of a new liquid phase microextraction method for the determination of several illicit drugs belonging to different pharmacological classes in oral fluid (OF) samples.

The workflow is very simple: the sample was collected through passive drool and centrifuged; then, it was processed by parallel artificial liquid membrane extraction (PALME) and analysed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) for the simultaneous identification and quantification of the selected analytes. PALME is an interesting liquid phase microextraction based on the use of a liquid support membrane which was first described and used in 2013 by Gjelstad et al[2]. Using this technique, it is possible to extract, from an aqueous biological sample, acid, basic or neutral molecules by creating a suitabile pH gradient that facilitates the mass transfer of uncharged analytes across the liquid membrane with organic support[3]. An experimental design approach has been applied for the identification of the operating conditions of each parameter that influences the extraction (extraction time, extraction pH, composition of the extracting solvent and acceptor solution, salt amount), and represented the best compromise for all analytes considered. The presented method proved to be suitable for analytes of different classes by using very small amounts of both organic solvents and biological samples, and so demonstrating to be an example of green chemistry. The method was subsequently validated following the guidelines of Scientific Working Group for Forensic Toxicology by evaluating parameters such as precision and accuracy, LOD and LOQ, linear dynamic range, matrix effect, recoveries.

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O5-FT

COMPARATIVE SPECTROSCOPY STUDIES OF KNOWN *VERSUS* NEW SYNTHETIC CANNABINOID FAMILIES

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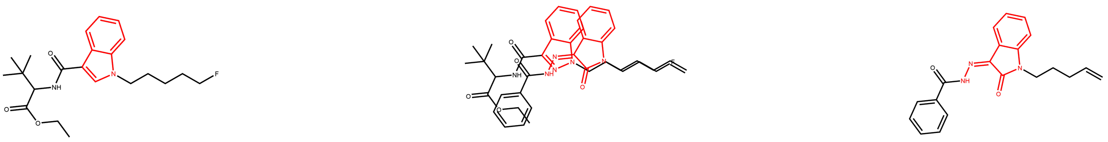
Identifying of psychoactive substances is, even today, a challenge[1]. The main families known so far are: synthetic cannabinoids, synthetic cathinones, opioids, tryptamines, piperazines, arylcyclohexylamines, and phenethylamines. In addition, targeted molecular modifications are able to yield new structures.

In the class of synthetic cannabinoids, which is the most widespread among drugs of abuse, the main reason that generates difficulties in identification procedures lies in the large number of possible combinations among the structural cores of the different families and of the potentially substitutable functional groups.



Indazole Isatinic Isatinic

Figure 1: Common families of synthetic cannabinoids.

Here we report a validated presumptive test to identify *in situ* synthetic cannabinoids belonging to the isatin family[2] in samples of seized plant material. The presumptive test has been developed targeting the identification of the structural core of this synthetic cannabinoid family.

In the same study, we have identified trace amounts of a substance which is structurally related to the psychoactive substance in the sized material.

Furthermore, UV spectroscopy studies have been carried out to develop chemo-selective reactions toward the constituents of the synthetic cannabinoid families, with the ultimate goal of succeeding in identifying, with a single test, which class the synthetic cannabinoids belong to.

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O6-FT

ORIGAMI PAPER-BASED DEVICE AS AN INEXPENSIVE TOOL FOR IDENTIFYING URINE ADULTERATION IN A FORENSIC TOXICOLOGY CONTEXT

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The relevance of the problem of urine tampering is well-known in forensic toxicology and sample dilution is the most used method to cheat toxicological controls.

The quantification of creatinine probably represents the most popular and used method for assessing urine integrity. Although most of the analytical methods offer adequate performances, at present, creatinine analysis requires laboratory instruments limiting the test at the collection site. This hinders the immediate interaction with the urine donor, which could be important to prevent claims of post-collection counterfeiting.

Since the first introduction by Whitesides et al.[1], the use of paper-based microfluidic devices (µPADs) for the development of rapid and on-site analytical devices has been extensively reported, also for forensic issues[2]. The fabrication procedure is based on patterning chromatography paper into hydrophilic channels by fabricating hydrophobic barriers, and addition of the reagent to the hydrophilic area. The sample is driven through the reagent zone as a result of paper capillarity without external assistance.

On these grounds, the goal of the present work was to develop a low-cost device, able to rapidly detect creatinine for identifying tampered urine samples. This presentation will provide details of the developed procedure which was conceived as a first-line screening potentially to be confirmed with laboratory instrumentation.

The proposed microfluidic device was designed as a three-dimensional origami pattern. The test was based on three colorimetric reactions for the detection of creatinine using picric acid, 3,5-dinitrobenzoic acid and, for the first time, Nessler's reagent. The urine sample is transferred without any treatment directly onto the hydrophilic portion of the paper, and colorimetric reactions are developed in few minutes. The color change is measured in terms of "RGB distance" by using simple and free software. The device was also validated for quantitative determinations in terms of accuracy and precision. The optimized method was tested on real urine samples using as reference, a clinical chemistry method performed on immunoassay instrument.

In conclusion, the perspective usefulness of paper-based microfluidics as a low-cost and easy to use technique in forensic toxicology will be presented with a specific focus on its possibilities of on-site analysis to prevent urine adulteration.

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O7-FT

VIRGIN AND PHOTODEGRADED MICROPLASTICS IMPACT THE INFLAMMATORY RESPONSE OF VASCULAR MUSCLE CELLS

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Microplastics (MPs) are being recognized as one of the main environmental problems due to their ubiquitous presence in various ecosystems[1]. Humans are continuously exposed to MPs and some recent findings suggest their role as a trigger for vascular inflammation, potentially worsening the cardiovascular patients' clinical condition[2]. Vascular smooth muscle cells (VSMCs) are the main component of medium and large arteries and play important roles in atherosclerosis. The present study investigates for the first time the effects of MPs on vascular muscle cell behaviour, metabolic activity, and pro-inflammatory state aiming to better clarify the MPs biomolecular modulation and their potential to generate a chemical fingerprint during exposure. Micronized powders of polystyrene (PS), high-density polyethylene (HDPE), and low-density polyethylene (LDPE), either virgin or artificially aged (4 weeks photodegradation at 40 °C and 750 W/m^2), were added (1 mg/mL) to Human Coronary Artery Smooth Muscle Cells (HCASMCs) culture media and left for 72 hours and 7 days. At these times, cell viability, intracellular ROS, IL-6, TNF-α, caspase-1 and volatile organic compounds (VOCs) were monitored. Virgin PS, LDPE, and HDPE showed a mild to moderate influence on cell viability, which was less evident for the 4-week-aged materials, suggesting a limited toxic effect of these polymers. On the contrary, virgin and aged PS showed an acute activation of inflammation mediated by caspase-1 and TNF-α just after 72 hours of incubation, conditions further exacerbated after 7 days. LDPE induced caspase-1 activation after 72 hours and a late response with IL-6 production after a week. Oxidative stress was potentiated after 72 hours in HCASMCs media when left in contact with aged LDPE and HDPE (for the latter, even after 7 days) and virgin HDPE. After 7 days, virgin HDPE stimulated an inflammatory response, mediated by both caspase-1 and IL-6. Pentane, acrolein, propanal, and hexanal resulted in the most important features ($p<0.05$) suggesting a potential link between VOCs emitted by cells incubated with MPs and the inflammatory response observed.

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O8-FT

HEPATIC CONCENTRATIONS OF RARE EARTH ELEMENTS IN DOMESTIC DOGS AND APENNINE WOLVES FROM CENTRAL ITALY

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The International Union of Pure and Applied Chemistry (IUPAC) defines rare earth elements (REEs) as 15 lanthanides with atomic numbers 57 to 71, and 2 transition elements, scandium (Sc), and yttrium (Y), with atomic numbers 21 and 39, respectively[1]. REEs are widely applied in medical and research facilities, pharmaceutical industries, mining and mineral processing, waste electronic, electrical equipment, high-technology industries, fertilizers, and livestock feeds[1]. Therefore, REEs are new contaminants of emerging concerns. However, due to the lack of exposure data on REE occurrence in environmental matrices, especially in European countries, it is still tricky to establish environmental background levels to assess the ecotoxicological risk related to REEs exposure. Herein, the evaluation of REEs' liver concentrations in domestic dogs (*Canis lupus familiaris*) (N=40), which are potentially exposed to the anthropogenic drivers of REEs pollution, compared with those found in the liver of Apennine wolves (*Canis lupus italicus*) (N=29), a valuable sentinel for the natural occurrence of REEs, will be presented. Liver samples from dogs and wolves were collected during diagnostic necropsies from carcasses, samples mineralization was performed by a microwave digestion system with single reaction chamber, and simultaneous determination of the presence of REEs was performed by Inductively Coupled Plasma Mass Spectrometer using standard mode for all rare earth elements except Sc which was acquired in KED (kinetic energy discrimination) mode. The Mann-Whitney U test showed the liver concentrations of cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, Sc, and Y in wolves with higher statistically significantly ($p<0.05$) compared to dogs. The results of the present study confirm the ability of REEs to accumulate in carnivore livers, suggesting the potential role of this species as an alternative bioindicator of animal and human exposure.

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O9-FT

THE ITALIAN TECHNICAL SPECIFICATION UNI/TS 11868:2022 FOR THE DETERMINATION OF SULPHITES IN MEAT

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Sulfiting agents (also known as sulphites) constitutes a class of chemical compounds - SO_2 releasers, widely used as additives in food industry. These additives may cause several adverse reactions in humans; thus, their use is strictly regulated. The reliability of the Monier-Williams method, reference standard traditionally used in food control, has been called into question by several authors due to repeatability and sensitivity drawbacks. In this study, a novel analytical method, based on ion chromatography with conductivity detection is proposed as new standard procedure for this type of determination. This protocol, already validated and published by the IZS Puglia and Basilicata, was submitted to a standardization procedure by the "Chemical Analysis of Meats" Working Group of the Italian Standardization Body (UNI). Three laboratories were involved in this inter-laboratory validation. The suitability of the following parameters was ascertained: method linearity ($r^2 > 0.999$) in the measurement range 8.0 – 160.0 mg kg^{-1}; selectivity; accuracy, as recovery and precision, equal to 97.7% and 5.9%, respectively, in compliance with the requirements of European Decision 808/2021/EC. ANOVA one-way test confirmed the homoscedasticity of data obtained by 3 laboratories ($p < 0.05$). The method was also submitted to Proficiency Test round, obtaining a z-score value of 0.3, confirming method suitability for accurate, sensitive and selective determinations of sulphites in fresh meats and meat products[1].

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The participation to the XXX Conference of the Analytical Chemistry Division was possible thanks to the research project code IZSPB 04/22 RC, financed by the Italian Ministry of Health.

O10-FT

THE POTENTIAL OF THE STABLE ISOTOPE RATIO ANALYSIS TO ENSURE THE AUTHENTICITY OF FOOD SUPPLEMENTS

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The analysis of the ratio between the heavy and light isotopes of the elements carbon ($^{13}C/^{12}C$), nitrogen ($^{15}N/^{14}N$), sulfur ($^{34}S/^{32}S$), oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) is well known for its power to discriminate the geographical origin and guarantee the authenticity of many agri-food products[1]. In recent years, the field of application of this technique has expanded to include nutraceuticals and pharmaceuticals, in particular in order to guarantee their natural origin. Chemically identical molecules are significantly different from an isotopic point of view due to the isotopic fractionation that occurs in different processes and reactions (biological, biochemical, physical, chemical, etc.) which generates unique isotopic signatures in the product synthesized by plants compared to that produced in the laboratory usually starting from fossil sources. Thanks to the coupling of isotopic mass spectrometry to liquid chromatography (LC-IRMS) and gas chromatography (GC-IRMS) it is now possible to discriminate between natural and/or synthetic origin not only of the bulk product but also of its specific components. The "Compound specific analysis" makes it possible to identify much more sophisticated frauds than in the past such as, for example, the addition of a single synthetic component to a natural substrate in order to artificially increase its strength. In this context, the $\delta^{13}C$ analysis is a suitable tool to discriminate between Monacolin K (contained in red yeast rice-based dietary supplements) and the marketed statin[2] and between natural L-theanine (extracted from *Camellia Sinensis)* and the biosynthetically produced one[3]. The isotope ratios of hydrogen and, in some cases, carbon exhibit significantly different ranges of variability between natural extracts (such as curcuminoids[4] and cannabidiols[5]) and their synthetic adulterant, allowing for the identification of not only the two origins, but also the fraudulent additions of synthetic products to the natural complex (spiked samples). The combination of GC-MS/MS and GC-IRMS is potentially useful for botanical classification between lavender (*Lavandula angostifolia*) and lavandin (*Lavandula hybrida*) essential oils thus representing an additional powerful tool for assessing the authenticity of commercial essential oils[6].

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Oral Ambienti e Beni Culturali

MICROWAVE-ASSISTED PRETREATMENT AND PY-GC-MS TO STUDY MICROPLASTICS AND CORRELATED POLLUTANTS

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Microplastic pollution is now acknowledged as a critical environmental and social issue. Nowadays an increasingly large number of studies is focused on determining microplastics (MPs) in different environmental matrices, and different analytical techniques have been applied and optimized for their analysis along with non-polymeric chemical species associated with MPs, such as additives, persistent organic pollutants and degradation products. Nevertheless, there is still a major lack of understanding of the most relevant mechanisms of interaction of these classes of pollutants with the environment or biota. Moreover, depending on the environmental matrix, sample preparation before analysis can require numerous and time-intensive steps.

In this work, we combined microwave-assisted extraction[1] and digestion, together with analytical pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC-MS), to simultaneously study and quantify MPs and different classes of pollutants in different environmental and biological samples. This approach can be potentially used to characterize and quantify MPs, soluble oxidation products of polymers, polymer additives (phthalate plasticizers), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs). The combination of microwave-assisted pretreatments and Py-GC-MS analysis represents an efficient and fast analytical strategy for the detection and quantitation of both polymeric and non-polymeric pollutants, contributing to the development of high-throughput methods that could be used for environmental monitoring.

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Acknowledgements:

The research was supported by University of Pisa Project PRA_2022_58 “Microwave assisted approaches for heritage science, environment, and energy” and by Milestone Srl (Sorisole, BG, Italy).

O2-ABC

SPECTROSCOPIC AND MULTI-SPECTRAL IMAGING ANALYSIS FOR THE ON-SITE CHARACTERISATION OF EGYPTIAN PAINTED CARTONNAGES FROM THE AGA KHAN III NECROPOLIS, ASWAN (EGYPT)

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The research displays some of the outcomes of the analytical investigation carried out at the Aga Khan III necropolis, in West Aswan (Egypt) in the scope of the EIMAWA mission (Egyptian-Italian Mission at West Aswan) during the MIASWAN (Mummies Investigations Anthropological & Scientific West Aswan) project.

This research aims to highlight the importance of the use of light, portable and suitable analytical instruments when it comes to the extreme conditions on-site during investigations of archaeological findings.

The study includes the preliminary assessment of the performance of the chosen analytical methods, the adaptation of the instruments' accessories to the on-site measurements and some of the results obtained during the two measurement campaigns carried out so far. The analytical equipment consisted of a portable ATR-FTIR spectrometer, a colorimeter provided with a visible reflectance accessory, a USB microscope with a 5 Megapixels sensor and an optional polarising filter, and a multispectral camera supplied with several excitation sources and specific filters, including the possibility of taking VIL (Visible Induced Luminescence) photographs. Therefore, some unreleased images from several vibrantly painted cartonnages and small objects (Figure 1) will be shown together with the first analytical results coming from this unique archaeological excavation site.

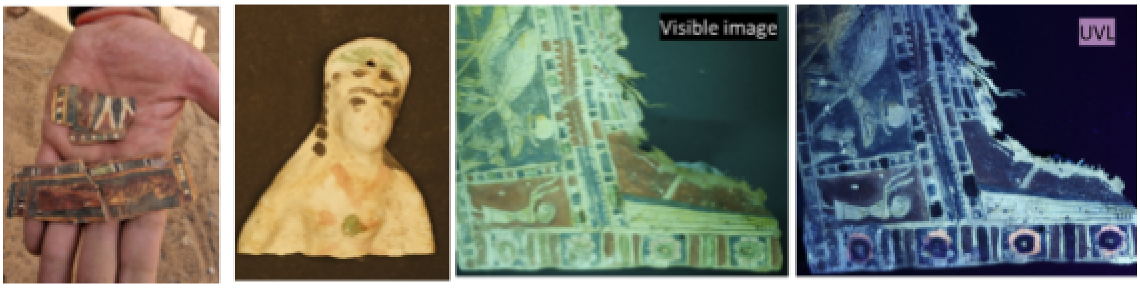

Figure 1: From left to right: small painted fragments of cartonnage, a decorated statuette, visible and UV induced luminescence images of a foot made of painted cartonnage.

ANALYTICAL APPROACHES FOR THE DETERMINATION OF THE CONCENTRATION OF AIR POLLUTANTS IN MUSEUM ENVIRONMENTS

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The monitoring of air quality in indoor environments such as museums is crucial for the preservation of the cultural heritage they contain[1]. In fact, several pollutants, released into the atmosphere by human activities and often transported by visitors inside the museums, can cause harmful effects on the materials composing the artworks. Within this context, in this study, different analytical approaches were used to assess the concentration of specific pollutants in the "Museo del Violino" in Cremona (Italy). Diverse passive air samplers were employed to determine the air concentration of nitrogen dioxide (NO_2), ammonia (NH_3), volatile organic compounds (acetic and formic acid, benzene, toluene, ethylbenzene, xylenes, and terpenes) during two sampling period (one in winter and the other in spring). Moreover, the particular matter level (PM10 and PM2.5) was constantly monitored with the Sensy sensor, developed by Sense Square (Salerno, Italy). For some pollutants of anthropogenic origin (NO_2 and PM10), it is important to verify that the determined concentration does not exceed the threshold values indicated as recommended concentration limits in museum environments (respectively 5 $\mu g/m^3$ and 20 $\mu g/m^3$)[2] to prevent the damage to the works of art. Other pollutants (acetic and formic acid, and terpenes) can be emitted from the wood of which violins are made, so their value may be indicative of the state of preservation of the work of art itself. In addition, some pollutants (NH_3 and PM) originate from the presence of the visitors themselves and their concentration must be evaluated and controlled in order to preserve the cultural heritage inside this museum.

The methodologies applied allowed us to highlight the strengths and weaknesses of the museum's exhibition practices, providing the curator with specific information for a better conservation of such unique and precious examples of Cremonese violin making.

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OPTIMIZATION OF EXTRACTION AND CHARACTERISATION OF ORGANIC RESIDUES IN POTSHERDS FROM “CANTIERE DELLE NAVI ANTICHE DI PISA”

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The archaeological site of “Cantiere delle Navi Antiche di Pisa” located in Pisa, has returned numerous ceramic artifacts in an excellent state of preservation. Ceramic has been one of the most common materials used in ancient societies for preparation, storage, cooking, and transport of several products[1]. It can preserve organic substances over time, whose characterization can provide several information on ancient population and disclose crucial hints about their daily life[2,3]. However, organic residues analysis is very complex due to the physical-chemical modification occurred overtime on the original material.

The research aims at the optimization of the analytical procedures employed for the extraction and analysis of organic residues from ceramic remains. Among the organic residues, particular focus was given to lipids. The analytical protocol has been optimized and primarily tested in the study of reference materials prepared by spiking virgin ceramic with standard solutions of triacylglicerides (TAGs) and fatty acids (FAs), and fresh oils. These were also subjected to artificial ageing to simulate the reaction occurred over time. Microwave-assisted extraction and experimental design strategies were employed to optimize the extraction procedure by investigating the effects of temperature and composition of the extraction mixture. Methods based on chromatography and mass spectrometry were used to chemically characterize the extracts. The optimized approach was subsequently used to study the organic residues from archaeological findings collected from the site.

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CHEMICAL CHARACTERIZATION OF FLINT ARCHAEOLOGICAL FINDS

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During the Paleolithic era, the mobility in Puglia represents an important archaeological problem aimed at understanding the settlement choices and the territorialization of human groups. The selection and management of lithic resources are indicators useful for reconstructing these choices through the study of the geographical provenance of the lithic artifacts. The work proposed here had as its objective the identification of the provenance of 36 archaeological finds of flint, 34 found at Grotta Torre dell'Alto (Nardò) and 2 in the Gargano plateau, through the comparison with a set of geological flints from different outcrops of Puglia and Basilicata[1]. Each sample was analyzed by Raman spectroscopy, Laser Ablation Inductively Coupled Plasma Mass Spectrometry and chemometric approaches. Raman spectroscopy was used as a fast and non-destructive technique that could provide clear information about the mineral composition[2]. LA-ICPMS was used for elemental characterization, selecting the most significant and least affected by diagenetic processes isotopes[3]. This technique guarantees high sensitivity and stability, low interference and LOD in the order of ppb[4]. Therefore, the integrated results obtained with both the techniques have provided a more complete characterization of the founds. Finally, the data obtained were subjected to multivariate statistical treatments, primarily Principal Components Analysis (PCA), to explore the geographical origin of the finds.

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O6-ABC

A MULTI-ANALYTICAL APPROACH FOR THE DETERMINATION OF THE FINENESS OF 12TH-13TH CENTURY EMILIA-ROMAGNA DENARII

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Nowadays, the most widely used analytical technique in the field of cultural heritage is X-ray Fluorescence (XRF)[1]. Although it has many advantages, it has one main limitation: XRF is not quantitative in the case of complex archaeological materials[2]. For this reason, it is usually necessary to calibrate the instrument with certified standards. In the absence of these, as in the case of ancient coins, one possibility may be to combine the results obtained from XRF with those derived from more robust techniques, such as Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

In this study, a batch of about 80 silver-copper coins (*denarii*) from Emilia-Romagna (Italy), minted in the period between the 12th and 13th centuries was analyzed to determine their fineness. The coins were micro-sampled and analyzed both with ICP-AES and XRF. The data obtained were used to build a calibration curve for evaluating the amount of silver in the coins. The validation set showed a good degree of reliability. The results achieved for the denarii of Ferrara agree with previous studies[3], with a decrease between the coins of the first type and the second type and an increase in silver content in the new *denarii* (Fig. 1). Therefore, the model obtained can be systematically applied for future non-destructive analyses to determine the silver concentrations of coins from the same era.

Moreover, the results of the application of multivariate analysis techniques on ICP-AES outputs and XRF spectra (Ag, Au, Bi, Cu, Fe, Ni, Pb) will be presented for assessing the presence of different forgeries.

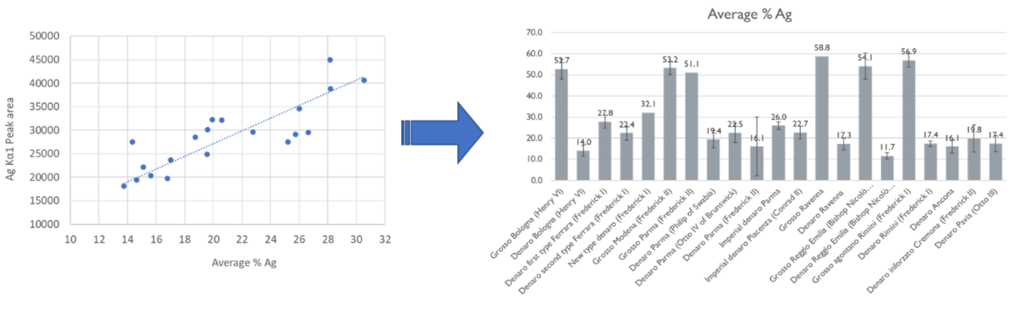

Figure 1: Left: line obtained by plotting the Ag concentrations provided by ICP-AES against XRF signals. Right: overall graph of silver trends for the different types of coins analysed.

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O7-ABC

GEL-SUPPORTED LIQUID EXTRACTION: BUILDING A BRIDGE BETWEEN NON-INVASIVE AND LABORATORY ANALYSES FOR THE IDENTIFICATION OF DYES

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The identification of organic dyes in paintings and textiles represents a challenge, because of their low concentration and the interference of inorganic materials in non-invasive and on-site analyses. Several approaches are available for the sensitive detection of these analytes in the laboratory, but the sampling is crucial with reference to the principles of preservation and non-invasiveness for conservation. Moving from recent research[1,2], the HybridGEL project exploits the versatility of Agar-gel and Nanorestore® substrates to conduct multi-analytical identification: the organic dyes are extracted directly from the art object by contact of a gel loaded with an extracting solution and then analysed by means of spectroscopic and/or chromatographic techniques[3,4]. The proposed methodology was tested on different dyes (madder, brazilwood, turmeric, indigo), in pictorial and textile mock-ups, evaluating different extraction conditions (e.g.: Agar-gel concentration, application time, extracting solution, etc.). The non-invasiveness of the procedure was evaluated by means of optical microscopy and colorimetry. Along with the compatibility with a preliminary multi-spectroscopic approach (UV-Vis-NIR spectroscopy, Surface Enhanced Raman Scattering spectroscopy), the efficiency of the extraction was evaluated in combination with a specifically designed clean-up for HPLC-MS analyses. The application to historical samples represented the final evidence of the potential of the methodology for its actual technology transfer.

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Acknowledgements:

The work was funded in the frame of Sapienza project “Bandi di Ateneo 2021” (“AGLAIA – Application of Gels supported Liquid extraction for Analysis and Identification of dyes in Artist matrices”).

O8-ABC

VIS-NIR HYPERSPECTRAL METHODS AND PHOTOLUMINESCENCE MA-IMAGING SYSTEMS FOR THE ASSESSMENT AND STUDY OF THE PERFORMANCE OF NEW CLEANING SYSTEMS FOR PAINTINGS

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The increasing demand related to the development of *ad hoc* materials for the restoration of cultural heritage requires the development of analytical protocols capable to evaluate in a quantitative way their performances.
In the frame of the international project GOGREEN and of the national funded project Superstar we are developing green materials for the cleaning of paintings, metals and street art heritage [1-3]. To propose to the conservation community the use of the new materials a methodology that allows easily to estimate the performance of the new methods in term of removal efficacy with respect to established systems is of the outmost importance.
It must be taken into account that conservator-restorers (CRs) usually do not have easy access to advanced scientific techniques. Therefore, it is equally necessary to develop analytical protocols that strike a balance among economic, practical, reliable result interpretation. Photoluminescence (PL) imaging and VIS-NIR hyperspectral camera are two methods that stands out in this perspective.
The two analytical systems have been tested on standard mock ups whose external varnished layer was cleaned using different cleaning strategies in order to find an easy to use system to evaluate the removal efficacy.
These first results pose the basis for set-up optimization in terms of acquisition conditions and data processing methods.

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Acknowledgements: :
Sustainable Preservation Strategies for Street Art (SuPerStAr) funded by MUR, PRIN;
Green Strategies To Conserve The Past And Preserve The Future Of Cultural Heritage (GOGREEN); financing institution: EUROPEAN COMMISSION (HORIZON EUROPE)

O9-ABC

INCREASING THE ACCURACY AND THE REPRODUCIBILITY OF THE PROCESSING METHOD FOR POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLERS

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Passive samplers are devices able to merge the sampling and the purification steps, directly in-situ. Among these, Polar Organic Chemical Integrative Samplers (POCIS) are widely diffused for water matrices[1]. They consist of a sorbent placed between two protective membranes held together by stainless-steel rings. Despite their advantages, POCIS are rarely used as a tool for regulated environmental studies[2], also due to the lack of a standardized processing method. While in a previous work of ours the elution step was studied in detail (to maximize analysis accuracy)[3], the sorbent transfer from the POCIS to a glass cartridge was not optimized. Variable amounts of ultra-pure water[2,3] or methanol[1] are generally employed to transfer the sorbent in a damp way, even though some of the more polar compounds are washed away[3]. A dry-transfer was previously proposed[4], but this could lead to stronger matrix effects. Thus, this work studied six POCIS deployed together in the Ligurian sea, evaluating the recoveries and matrix effects of 38 target analytes ($\log D_{pH=7}$ -3.8 ÷ 6.8). Two of these POCIS were processed as usually[3], while the remaining four were dried overnight and then transferred into a glass cartridge using only a stainless-steel spatula. The sorbent of two of the four dry-transferred POCIS was spiked with a known amount of the analytes. Then, prior to the elution[3], 5 mL of water were used to wash the sorbent. This water was recovered and processed through a Salt-Assisted Liquid-Liquid Extraction (SALLE) and analysed along with the sorbent eluates by LC-MS/MS. Each extract was divided in aliquots, properly diluted with or without spike, allowing to assess analytes' recovery and matrix effect. Through SALLE, almost all the analytes were recovered from the water. Yet only acesulfame and chlormequat were significantly washed from the spiked sorbent, thus SALLE resulted useful only for these two analytes. The new dry-transfer procedure allowed better recoveries of several polar analytes (e.g. salbutamol recovery improved from 20%[3] to ≃60%), while matrix effects were not substantially different from the usual method, resulting negligible (80-120%) for 30 out of the 38 target analytes. The proposed procedure is desirable to improve compounds detectability and method reproducibility.

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CHLORINATED AND BROMINATED PERSISTENT POLLUTANTS IN SEA TURTLES OF ADRIATIC AREA: A MULTI-RESIDUAL APPROACH

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Persistent organic pollutants (POPs) are organic substances that, thanks to their stable chemical structure, strongly resist to photolytic and biological degradation. They persist in the environment and accumulate in living organisms being a concern to both humans and wildlife because of their toxicity. POPs include a variety of compounds such as dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecanes (HBCDDs).

The contamination of aquatic environment by bioaccumulation of POPs and the effects on marine life have become matters of concern. In this scenario the European Commission drafted the Marine Strategy Framework Directive (MSFD)[1] highlighting the importance of monitoring and assessing the water quality. Among marine species, turtles have been widely used as a target indicator for POPs exposure because of their longevity together with the carnivorous behavior that places this species at high trophic level in marine food web. *Caretta caretta* is the most common species of sea turtle in the Mediterranean Sea, using the Italian coasts for nesting and feeding ground.

In this study, the contamination levels of 44 loggerhead sea turtles (*C. Caretta*) stranded along central Adriatic coast were evaluated. A multi-residue method was applied to determine trace levels of chlorinated (PCDD/Fs, DL-PCBs and NDL-PCBs)[2] and brominated (PBDEs and HBCDDs) persistent pollutants in liver and fat tissues. The analytical methodology was based on isotope dilution technique, followed by gas or liquid chromatography coupled with high resolution mass spectrometry detection. A potential correlation between the contamination levels with sex and size in terms of curved carapace length (CCL) was assessed. The multi-residual approach proved to be a more rapid and cost-effective method usable for future monitoring studies.

Most of these contaminants were found in both liver and fat tissues, corroborating the evidence that these compounds are easily bioaccumulated in sea turtles.

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O11-ABC

OCCURRENCE OF PER- AND POLYFLUORINATED ALKYL SUBSTANCES IN WASTEWATER TREATMENT PLANTS IN NORTHERN ITALY.

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Wastewater treatment plants (WWTPs) are known to be relevant input sources of per- and polyfluoroalkyl substances (PFAS) in the aquatic environment[1]. This study aimed to investigate the occurrence, fate, and seasonal variability of twenty-five PFAS in four municipal WWTP (A, B, C, and D) surrounding the city of Milan (Italy). Composite 24-h wastewater samples were collected seasonally, from July 2021 to February 2022, from influents and effluents of the four WWTPs[2]. PFAS were extracted by solid-phase extraction and analysed by an ultra-HPLC system coupled to a triple quadrupole mass spectrometer. Concentrations ranging 24.1-66.9 $\mu g\ L^{-1}$ and 13.4-107 $\mu g\ L^{-1}$ were detected in influent and effluent wastewater samples, respectively. Perfluoropentanoic acid was the most abundant (1.91-30.0 $\mu g\ L^{-1}$) in influent samples, whereas perfluorobutane sulfonic acid predominated (0.80-66.1 $\mu g\ L^{-1}$) in effluent samples. Sludge samples were also collected, extracted according to EPA 3550C 2007 and EPA 8327 2021, and analysed. PFOA was detected in plant A at concentrations in the range of 96.6-165 ng kg^{-1} dw in primary sludge samples and 98.6-440 ng kg^{-1} dw in secondary treatment sludge samples. The removal efficiency of total PFAS varied between 6% and 96%. However, an increase of PFAS concentrations was observed from influents to effluents for plant D (during July and October), plant A (during October and May), and plant C (during May) indicating that biotransformation of PFAS precursors can occur during biological treatments. This was supported by the observed increase in concentrations of PFOA from primary to secondary treatment sludge samples in plant A. Moreover, the plant operating at shorter hydraulic retention times (plant D) showed lower removal efficiency (<45%). Seasonal variation of PFAS in influent and effluent appears rather low and more likely due to pulse release instead of seasonal factors.

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Acknowledgements:
A special thanks to Gruppo CAP for the sampling campaigns.

O12-ABC

CHEMICAL CHARACTERIZATION AND SPECIATION OF THE SOLUBLE FRACTION OF ARCTIC PM_{10}

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The soluble fraction of atmospheric particulate matter can affect the chemistry of the atmospheric aqueous phase, such as raindrops, clouds, fog, and ice particles. Compounds such as transition metal ions are known for their (photo-)catalytic behaviour and their tendency to form complexes in solution[1]. This study was focused on the analysis of the soluble fraction of Arctic PM_{10} samples collected at Ny-Ålesund (Svalbard Islands) in 2012. The concentrations of Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, formate, acetate, malonate, and oxalate in water were determined by ICP-OES, SF-ICP-MS, and ion chromatography. Principal component analysis was used to describe the similitudes and seasonal differences between samples by the variability in the concentrations of the components. Speciation models were applied to define the major species that were formed in solution as a function of pH using the software PyEs[2]. The model highlighted *(i)* the presence of the main cations such as Na^+, K^+, Mg^{2+}, and Ca^{2+} in the form of aquoions through all of the investigated pH range (2-10); *(ii)* Cu^{2+}, Zn^{2+}, and in particular Fe^{3+} and Al^{3+} are mostly present in their hydrolytic forms; *(iii)* Al^{3+}, Fe^{3+}, and Cu^{2+} have solid hydrolytic species that precipitate at pH slightly higher than neutrality (Figure 1). Moreover, these metals show interesting interactions with oxalate and sulphate ions. The speciation models were also run by considering the seasonal variability of the concentration of the components and at higher concentration level to better simulate the real environmental conditions. In fact, the water associated to the particulate at low temperatures is very scarce. The results highlighted the main role of oxalate as ligand in solution. The determination of thermodynamic constants at lower temperatures will be necessary to better simulate the species distribution.

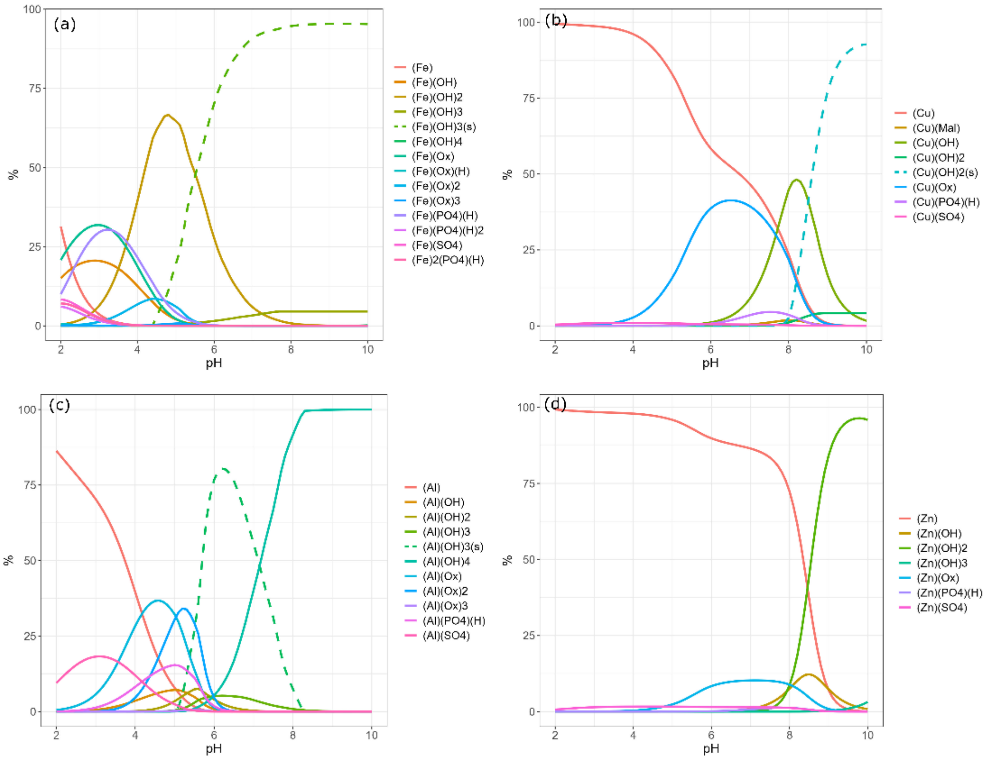

Figure 1: Species distribution diagrams of (a) Fe^{3+}, (b) Cu^{2+}, (c) Al^{3+}, and (d) Zn^{2+} occurring in the soluble fraction of Arctic PM_{10} collected in 2012 as a function of pH.

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O13-ABC

A SIMPLE TWO-MEDIA DEGRADATION MODEL TO EVELAUATE THE ENVIRONMENTAL FATE OF 4-ISOBUTYLACETOPHENONE, A SEMIVOLATILE TRANSFORMATION PRODUCT OF IBUPROFEN

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The partitioning of semivolatile contaminants between surface waters and the atmosphere is an important process that influences their fate and transport[1]. We proposed a simple methodology that combines experimental data and modelling to investigate the degradation of 4-Isobutylacetophenone (IBAP) in a two-phase system (surface water and atmosphere). IBAP is a semivolatile and toxic transformation product of the widely use drug ibuprofen (IBP), photochemically formed in sunlit surface waters.[2] The atmospheric behaviour of IBAP would mainly be characterized by its degradation with OH radicals (degradation by NO_3 radicals or direct photolysis would be negligible). Furthermore, the gas-phase reactivity of IBAP with OH is faster compared to the likely kinetics of volatilization from aqueous systems. Therefore, it would be extremely difficult to detect gas-phase IBAP. Nevertheless, up to 60% of IBAP occurring in a deep and DOC-rich water body might be degraded via volatilization, and subsequent reaction with gas-phase OH. In conclusion, the present study suggests that the gas-phase chemistry of the semivolatile organic compounds initially occurring in surface waters (like IBAP) is potentially very important in some environmental conditions.

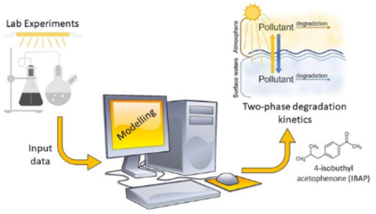

Figure 1: Description of the experimental/modelling approach used to evaluate the IBAP environmental fate

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Acknowledgements:

This research has received funding from the Project CH4.0 under the MUR program "Dipartimenti di Eccellenza 2023-2027" (CUP: D13C22003520001).

O14-ABC

EVALUATION OF SORPTION ABILITY OF SOY PROTEIN MICROSPONGES TOWARDS Pb^{2+} IONS

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In the last decade, protein-based materials are emerging as promising adsorbents of toxic metal ions from polluted waters[1-3]. Indeed, they have the main characteristics of the model adsorbent: i) high availability of the raw material, ii) cost-effective, iii) biocompatibility, iv) high density of binding sites, v) ease to prepare.

In this work, we produced protein microsponges based on Soy Protein Isolate (SPI) and tested them as adsorbent of Pb^{2+} ions. SPI derives from the soybean oil production industry, has an isoelectric point in the pH range 4 - 5 and two major fractions: the trimer, glycoprotein β-conglycinin (7S) and the hexamer glycinin (11S)[4]. The microsponges have amyloid-like molecular structures and were prepared incubating SPI aqueous solutions at high temperature and at two different pHs, namely pH 5 and pH 9, which are close and away from the isoelectric point of protein, respectively. The solution conditions of SPI incubation affect the polarity and the water accessibility of microsponges, changing their metal binding affinity. The two SPI adsorbents were characterized by various spectroscopic techniques such as micro- and ATR-FTIR and FLIM analysis while their adsorption behaviour towards Pb^{2+} ions was studied carrying out batch isotherm and kinetic experiments at different experimental conditions. The Pb^{2+} ion concentration in the collected solutions was measured through Differential Pulse Anodic Stripping Voltammetry (DP-ASV) technique and several kinetic and isotherm adsorption models were used to process the experimental data. In addition, lead removal experiments using column-supported SPI microsponges were carried out to analyse the adsorption capacity under dynamic conditions and evaluate the recycle and the reuse of the microsponges.

SPI microsponges successfully removed Pb^{2+} ions from aqueous environments, also demonstrating a high degree of recycling.

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ONLINE AUTOMATED MEASUREMENT AND OPTIMIZATION OF H_2O_2 CONCENTRATION USING ARDUINO ROBOT.

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Analytical chemistry procedures are often time and reagents demanding and generate relevant amounts of wastes to be treated. To improve their sustainability, Green Analytical Chemistry principles promote the minimization of samples size and number, the in situ measurements, and the use of automated and miniaturized methods. Automated systems refer to the use of electronic devices such as sensors and actuators to control analytical processes in an accurate and reproducible way and reducing the manual intervention. One of the most widely employed electronic devices in homemade automatic systems are Arduino boards. An innovative and so far unexplored research field is the use of Arduino devices for the monitoring and control of Advanced Oxidation Processes (AOPs), employed for the removal of organic contaminants from water. Among AOPs, the photo-Fenton process is one of the most promising ones and it relies on the formation of ·OH from the reaction between H_2O_2 and Fe(II) ions. The use of light has been proven to accelerate Fe(II) regeneration, the principal specie responsible for H_2O_2 decomposition yielding ·OH formation. The correct dosing of H_2O_2 is a crucial point in this process, not only as a matter of cost, but also because it can be the rate-limiting reagent in contaminants degradation. This highlights the need for fast and reliable H_2O_2 determination and automatic dosing to optimize the photo-Fenton pollutant degradation.

In this work a cheap Arduino self-assembled robot was employed for the online monitoring of the H_2O_2 consumption and for the optimization of its dosing during the photo-Fenton degradation of caffeine and paracetamol, selected as model contaminants of emerging concern. The obtained results were compared in terms of LOD and LOQ with H_2O_2 measurements performed manually using a laboratory UV-Vis spectrophotometry, evidencing that better performances were obtained when using the robot. To fulfil the Green Analytical Chemistry principle of minimizing the number of samples, design of experiments was applied to study the effect of experimental conditions on caffeine and paracetamol degradation.

Acknowledgements:
Authors acknowledge support from the Project CH4.0 under the MUR program "Dipartimenti di Eccellenza 2023-2027" (CUP: D13C22003520001).

O16-ABC

THERMAL DEGRADATION CHEMISTRY OF LIPIDS: AN AGEING STUDY ON EVOO SAMPLES BY MEANS OF GAS AND LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY TECHNIQUES

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Artificial ageing tests can provide key elements to study the formation of characteristic degradation compounds and better address the origin of organic archaeological remains, such as animal fats and plant oils resulting partially or totally altered over time[1].
In the present research, in-lab thermal-oxidative treatments have been carried out on extra-virgin olive oils (EVOOs), traditionally used in Mediterranean ancient societies, for the purpose of simulating the natural degradation of the lipid matter.
In order to obtain meaningful data, several *monocultivars* of EVOO samples from different Italian regions (Sicily, Tuscany, Apulia, Lazio, Liguria) and Spain, were selected. The ageing of lipids was performed at 120°C for three weeks[2]. Subsequently, thermal degradation products such as medium- and long-chain fatty acids, (α,ω)-dicarboxylic acids, ketons, lactones, and esters were investigated by using gas chromatography-mass spectrometry (GC-MS) and gas chromatography-flame ionization detection (GC-FID) techniques. About the identity of intact lipids, including oxidized lipid species, non-aqueous reversed phase high-performance liquid chromatography (RP-HPLC) coupled to APCI mass spectrometry.
The analytical methodologies here proposed, can be helpful in archaeological contexts, to identify specific “archaeological biomarkers” and unveil crucial hints about the daily life of ancient societies.

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Acknowledgements: The authors acknowledge Merck Life Science and Shimadzu Corporations for the continuous support.

O17-ABC

CHARACTERIZATION OF ORGANIC MATTER IN SOIL WITH BIOPLASTICS AND QUANTIFICATION OF AGED BIOPLASTICS BY PY-GC-MS AND EGA-MS

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Contamination of the environment with plastic debris is one of the major environmental problems on a global scale and concerns are constantly growing with increasing demand for substituting conventional plastics with bioplastics. Bioplastics are materials that are biobased and/or biodegradable, but not necessarily both. It was estimated that almost half of bio-based polymers were not susceptible to biological decomposition in the environment[1]. Therefore, non-biodegradable oil-based plastics should be gradually replaced by bio-based biodegradable plastics to prevent the contamination of the environment with plastic debris. However, for biodegradable polymers to completely decompose/degrade, they require specific environmental conditions that are rarely met in natural ecosystems, leading to the rapid formation of micro-bioplastics. Moreover, studies have reported significantly higher effects on soil microbial communities and diversity, on plants' health and growth due to bioplastics[2]. Little information is available regarding their environmental occurrence and potential effects on the soil compartment.

The present study aimed to assess the effect of biodegradable bioplastics on the characteristics of soil organic matter (SOM) and dissolved organic matter (DOM). The focus was given to agricultural soil obtained by a laboratory experiment at different bioplastics load, identifying and quantifying micro-bioplastics generated in the soil during the experiment by pyrolysis-GC-MS (Py-GC-MS) analysis. In order to characterize the effect of commercial biodegradable plastics, common polylactic acid (PLA) and starch-based biodegradable polymers were incubated in an agricultural soil for 90 days. Concerning the stability of bioplastics under environmental conditions, aged bioplastic was characterized by Py-GC-MS and evolved gas analysis coupled to mass spectrometry (EGA-MS). This study provides insights into the environmental occurrence and potential impacts of bioplastic showing the results of a 90-day laboratory-scale incubation experiment. The results of the thermoanalytical investigation by Py-GC-MS and EGA-MS techniques are consistent in highlighting no significant changes in the composition of bioplastics due to the aging process. Furthermore, the Py-GC-MS results showed the generation of micro-bioplastics and that bioplastic residues can affect soil DOM.

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Oral Green Chemistry

A NEW POSSIBLE APPLICATION OF KARKADE' EXTRACT USING RAPID SOLID-LIQUID EXTRACTION (RSLDE)

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Hibiscus is an aqueous extract obtained from hibiscus flowers (*Hibiscus sabdariffa*), rich in bioactive compounds, especially polyphenols, vitamins C and A. Therefore, *Hibiscus* extract shows antioxidant, anti-inflammatory and diuretic properties. In this work, the karkadè extract was obtained using a new technology called Rapid Solid–Liquid Dynamic Extraction (RSLDE) also known as Naviglio extractor[1,2]. RSLDE can be used to extract bioactive compounds from agro-industrial waste, such as essential oils from orange peels or polyphenols, or oleuropein and hydroxytyrosol from olive leaves. Additionally, polycaprolactone (PCL) foams were used to understand the mechanism of release of bioactive compounds, using high pressure carbon dioxide as blowing agent[3]. PCL is a biocompatible and biodegradable aliphatic polyester that is bioresorbable and nontoxic for living organisms. Therefore, *Hibiscus* flowers were extracted in stabilized water containing 0.15% citric acid and 0.2% potassium sorbate for 6 hours. At first, aqueous extract was analyzed in terms of yield extraction and antioxidant properties. Then, karkadè extract was loaded into foams to evaluate its encapsulation efficiency and antioxidant activity. According to the best operating conditions, empty foams with a density of 0.18 g/cm^3 were produced at 100 bar, 45°C and a sorption time of 60 min, with an expansion ratio up to 637 %. Loaded foams were then prepared: encapsulation efficiency of karkadè extract ranged between 83 and 97%. The antioxidant power, significantly reduced by 70-80%, was not due to the process itself, neither to the preparation of foam precursor (disk or pellet), but to the interactions among the several compounds extracted in karkadè. This was confirmed by the foaming of the single gallic acid, that is one of the karkadè components, that instead resulted only in 30% antioxidant power inhibition.

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Acknowledgements:

I would like to thank the researchers of the Department of Chemical, Materials and Industrial Production Engineering, University of Naples Federico II, Piazzale V. Tecchio, 80, 80125 Naples, Italy for the collaboration.

RETENTION PROPERTIES OF A POROUS GRAPHITIC CARBON COLUMN AS STATIONARY PHASE IN SUPERCRITICAL FLUID CHROMATOGRAPHY

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Retention on Porous Graphitic Carbon (PGC) is found to occur through a combination of factors with interactions between the mobile phase and analytes promoting or discouraging retention. Nonpolar analytes interact with the PGC surface via dispersive forces while polar ones are retained via charge induction on the polarizable PGC surface. The mobile phase is a major determinant of retention because it influences the ionization state of both analytes and the PGC surface.

While many applications have been developed in liquid chromatography (HPLC), there are only few examples of the use of PGC in supercritical fluid chromatography (SFC), and more work is foreseeable to fully understand and exploit its capabilities.

In this research a novel PGC stationary phase was investigated, consisting of 2.7 μm particles, (Supel Carbon LC, 3.0 mm I.D.) for the separation of analytes differing in polarity, size, and shape.

Changes in temperature has less effect of retention than modifier concentration, but sometimes resulted in significant shifts in selectivity. Moreover, it was found that when using higher modifier concentration, the effect of both outlet pressure and temperature changed, probably because the modifier concentration becomes even more dominant over the density of the mobile phase.

It is noteworthy that, given the higher diffusion coefficients of the solutes in SFC, method optimization requires less time and solvent consumption, compared to HPLC.

Acknowledgements:
The authors are grateful to Merck Life Science and Shimadzu Europa for their continuous support.

O3-GC

A GREEN EXTRACTION METHOD BASED ON CARBON NITRIDE SORBENT FOR THE SIMULTANEOUS DETERMINATION OF FREE AND CONJUGATED ESTROGENS IN MILK

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Among endocrine-disrupting chemicals (EDCs), an important class consists of estrogens which can interfere with the development, reproduction, metabolism, and behavior in various animal species, including humans. The occasional presence of relatively high amounts of natural estrogens in milk and milk derivatives and the abusive or illegal use of synthetic estrogens in dairy practices have become causes for concern since the intake of these hormones is associated with illnesses or disorders[1]. This study[2] proposes a quick and green method based on carbon nitride sorbent to extract six free and five conjugated estrogens from milk samples simultaneously. After the matrix solid phase extraction optimization, extraction was carried out using this magnetic material after a previous deproteinization step. Separation, determination, and quantification of the target analytes were achieved by ultra-high-performance liquid chromatography coupled with triple quadrupole-tandem mass spectrometry. The methodology was validated in 6 milk samples. The LODs and LOQs for free and conjugated estrogens investigated were in the range of 0.01–0.1 ng mL^{-1}. The recoveries of estrogens (concentration range of 0.5–10 ng mL^{-1}) from milk samples were in the range of 89–100%, with standard deviations ranging between 1 and 3%. The method was successfully applied to milk samples leading to the identification of estrone, 17-α-estradiol, 17-β-estradiol, 17β-estradiol-3-glucuronide, estrone-3-sulfate, 17β-estradiol-3, 17β-disulfate, 17β-estradiol- 3-sulfate.

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A BIOACTIVE CHITOSAN-BASED PACKAGING FOR FOOD PRESERVATION

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This work focuses on the production of a bioactive film designed for food wrapping applications by using chitosan synthesized from fish waste (crustaceans), and plant extracts. The synthesis of chitosan involved two distinct approaches aiming at converting chitin into chitosan: i) chemical - deproteinization and deacetylation of the discarded material; ii) fermentative - microbial fermentation by using *Bacillus subtilis* and *Serratia marcescens* strains. The film has been obtained by stratification of a thin layer (range of thickness, 150-300 μm) that can effectively wrap food products. Successively, the biofilm has been subjected to mechanical testing: break stress, elongation at break, hardness, and glass transition temperature. Microbiological tests have been performed on semi-hard cheese samples wrapped with the chitosan-based biofilm (treated group, T) and with conventional PVC film (control group, C) by analyzing the microbial load, such as mesophilic and acidophilus microbia, to determine the biofilm's effectiveness in inhibiting spoilage. In parallel with the microbiological testing the aromatic fraction of the wrapped cheese samples (both C and T groups) has been monitored by means of SPME-GC-MS technique, in order to evaluate any potential changes in the flavor profile. This analysis provided valuable information regarding the impact of the chitosan-based biofilm on the sensory quality and aroma stability of the wrapped food products. The study contributes to the advancement of sustainable and functional food packaging materials with potential applications in the food industry.

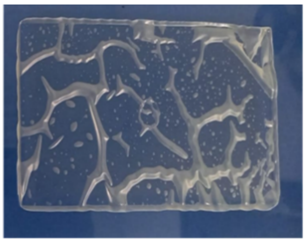

Figure 1: the novel chitosan-based biofilm

GRAPHENE OXIDE AND CARBON NANOTUBES NANOCOMPOSITE, BASED ON RECYCLED POLYLACTIC ACID, FOR THE MAGNETIC SOLID PHASE EXTRACTION OF XENOBIOTICS FROM URINE

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Over the last few years, the attention of the scientific community has been devoted to the development of procedures, materials, and recycling operations to make analytical chemistry more and more sustainable. Such considerations are even more relevant in the field of sample preparation. In particular, materials used for solid phase extraction (SPE) are, usually, very expensive and synthetized with Brown Chemistry procedures, not paying attention to sustainability aspects. In this study, nanocomposite sorbents were prepared through the recycling of polylactic acid (PLA) from waste materials such as PLA sheets, recovered from tobacco products for the non-burning technology. A washing procedure was optimized to regenerate PLA. Among a wide group of solvents tested, tetrahydrofuran (THF) was chosen to dissolve the regenerated PLA so to obtain a saturated solution. Magnetic nanoparticles, made up of Fe_4O_3, were prepared from aqueous solution 0.5 M in HCl of $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}nH_2O$ (2:1 molar ratio). This solution was added drop by drop to an aqueous solution 1.25 M in NaOH. A black precipitate of magnetic Fe_3O_4 particles was formed after the addition. The nanoparticles were added to the PLA organic solution together with an active carbon-based material, the last one to assist the extraction of analytes from the matrix. Carbon nanotubes (CNTs) and graphene oxide (GO) were selected as coadjutants for the extraction. With the technique of the emulsion precipitation, the three-component organic phase was combined with a water solution, saturated with sodium chloride. As a result of the salting out effect, the organic and aqueous phases were immiscible, and a cloudy solution was formed under magnetic stirring. The drop-by-drop addition of water to the emulsion broke the emulsion and promoted the precipitation of PLA in the form of nanospheres. A complete characterization study was performed via SEM and TGA analysis, as well as FTIR for the qualitative confirmation of the obtained material composition. PLA@CNTs and PLA@GO were tested as sorbents for the magnetic-SPE. These materials were tested with a wide group of pollutants (pesticides, drugs, ecc.) of different polarity and polarizability, from urine samples.

Ideal peculiarities of such composites are the sustainability (recyclability of the PLA and its complete biodegradability) and the simplicity of their realization. The perfect compatibility of PLA with different secondary components enables to control the adsorption capabilities of the material depending on specific requirements. The entire method was validated in accordance with the main criteria established by FDA guidelines. For CNTs and GO, partially overlapping performances were registered. In both cases, it was possible to obtain recoveries greater than 80% for a fair number of analytes, with a good level of precision. The matrix effect for the considered samples was lower than 20%.

EVALUATION OF TRACE ODOUR COMPONENTS BY MEANS OF A NOVEL 3D GC SYSTEM COUPLED TO OLPHACTOMETRIC, FID AND MS DETECTION

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This study describes the effectiveness of a multidimensional gas chromatographic system exploiting three gas chromatographic systems coupled to an olfactometric port and to a simultaneous FID/MS system (TDGC-O-FID/MS) for the identification, quantification and odour evaluation of trace components in essential oils. The reliable detection of trace odour active components from complex matrices represents a challenging purpose and trained panellists are required. To compare the capabilities of conventional and multidimensional GC-O approaches, a sulphur compound with a low-odour threshold was used, namely, p-mentha-8-thiol-3-one, characterised by a tenacious sulphurous odour type, which can be described as catty and black currant. The odour threshold determined exploiting monodimensional GC-O employing a micro-bore column was around 10 ppm. The same experiment employing a wide-bore column was not successful since the reduced efficiency of the column did not provide the separation of the target compound. On the contrary, the TDGC approach, exploiting a set of three wide-bore columns, provided an improved sensitivity of 10 ppb. The combination of the heart cut method and the use of wide-bore columns allowed to reach the goal of a high sample capacity coupled to high efficiency levels. This approach represents an effective tool to guarantee an enhanced odour evaluation at ppb level. Moreover, the possibility to switch between the olfactometric port and the simultaneous FID/MS detections allowed the quali-quantitative evaluation of the target component.

Acknowledgements:
The authors gratefully acknowledge the Shimadzu Corporation and Merck Life Science for their continuous support.

O7-GC

RECYCLE MATERIALS BY DEVELOPING ALTERNATIVE LOW ENVIRONMENTAL FOOTPRINT SENSORS

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In order to meet the demand for quick and simple tests in various application domains, flexible screen-printed technology in combination with the use of nano/materials coating increasing electrode functions improved the production of extremely sensitive electrochemical sensors[1,2]. However, due to the large-scale production and disposable and single-use nature of these devices, their environmental footprint should be taken into careful consideration. Herein, the innovative reuse of post-consumer plastics as an alternative substrate coupled with biochar as an environmentally friendly and cost-effective modifier are described as sustainable alternatives to produce robust electrochemical sensors. The good printability of reused plastic with graphite inks despite chemical heterogeneity, different crystallinity, and surface roughness was demonstrated using Atomic Force Microscopy and Attenuated Total Reflection Fourier Transform Infrared spectroscopy. Functionalization with a biochar-multilayer system enabled the fabrication of highly performing electrochemical sensors tested for nitrites detection in water having a limit of detection and limit of quantification of 3.3 nM and 10.3 nM, respectively, with a linear range spanning from 0.01 to 500 μM, and good reproducibility (RSD% 8%). This work lays a foundation for repurposing end-of-life plastics for the electronics industry and presents a customizable reuse strategy aimed to reduce waste and leakage into the natural environment.

Figure 1: Screen-printed electrode based on post-consumer plastics.

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Acknowledgements:

The authors thanks G. Rea, L. Cerri, G. Leo of Instutute of Crystollaphy and Istitute of Nanostructure materials (CNR), P. Mantegazza, L. Severini, C. Mazzuca of Chemical Sciences and Technologies, University of Rome Tor Vergata for Atomic Force Microscopy and Attenuated Total Reflection Fourier Transform Infrared spectroscopy and Dr K. Carbone (CREA Research Centre for Olive, Fruit and Citrus Crops) for biochar. The authors also acknowledge the Regione Lazio funded project FACILE, grant n. 85-2017-15256 for implementing this scientific network.

O8-GC

CONTINUOUS PHOTOCATALYTIC SYSTEM FOR WATER REMEDIATION: A LAB-SCALE PROTOTYPE

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In the last years a large number of new contaminants have affected the quality of both superficial and underground water around the globe. The presence of these pollutants it's difficult to evaluate due to their low concentration and the complexity of detection. The growing attention to emerging contaminants (EC) is leading to a change in the water quality and aquatic environment definition, which must increasingly respond to assessments of the protection of human health and the environment. The increase in the human life expectancy coupled with the rise in population increased the use of pharmaceuticals, and thus, intensify the presence of antibiotics, analgesics, anti-inflammatory, antihistaminic, antiepileptic, and other type of drugs in aquatic environments: a long list that is continuously updated. Unfortunately, today's WWTPs are unable to effectively remove these compounds and therefore many pharmaceuticals end up in aquatic ecosystems, inducing problems such as toxicity and antibiotic resistance. Therefore, it is important to study and develop new strategies and innovative technologies for water remediation. A possible approach for polluted waters remediation has been demonstrated to be the use of advanced oxidation processes (AOP)[1]. AOPs are based on the ability to photoproduce species of free radicals, such as ($^{\cdot}$OH), which being a strong oxidant characterized by an oxidation potential equal to $E° = +2.1$ V vs. NHE allows the oxidation of a variety of organic substances leading to their mineralization. In this work, a laboratory-scale plant for the remediation of pharmaceuticals-contaminated water was employed. The photodegradation studies were initially conducted using the batch method, and then moved on to the continuous system. The photocatalyst used was WO_3; in the continuous system the catalyst was immobilized on the surface of the glass spheres. LC/MS analysis was performed to evaluate degradation kinetics, by-product formation and to assess the degradation pathway.

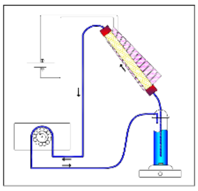

Figure 1. Continuous photocatalytic system

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Oral Chemiometria

SINGLE-MOLECULE BIOELECTRONIC SENSOR: IMPROVING RELIABILITY WITH CHEMOMETRIC APPROACHES

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Digitizing biomarkers analysis by quantifying them at the single-molecule level is the new frontier for advancing the science of precision health. The enhancement of the technical capabilities of bioelectronics systems, by giving clinicians the possibility to rely on biomarkers quantifications down to the single-molecule, holds the potential to revolutionize the way healthcare is provided. Such an analytical tool will indeed enable clinicians to associate a biomarker tiniest increase to the progression of a disease, particularly at its early stage.[1] Eventually, physicians will be able to identify the very moment in which the illness state begins. Such an occurrence will enormously enhance their ability of curing diseases by supporting better prognosis and permitting the application of precise treatment methods. The single molecule bio-electronic smart system array for clinical testing - SiMBiT - technology has been developed within the blooming field of precision medicine, leveraging on the single molecule with large transistor (SiMoT)[2] lab-based technology that can perform single-molecule detection of both proteins and DNA bio-markers.[3,4] Specifically, the SiMBiT technology has lately developed the SiMoT lab-based device into a cost-effective portable prototype multiplexing array that integrates, with a modular approach, standard components and interfaces with novel materials and exhibits enhanced sensing capabilities. The SiMBiT prototype has proven its potency in early detection of pancreatic cancer, being capable to discriminate among low-grade and high-grade mucinous cyst's lesions in peripheral biofluids, such as plasma samples. In this perspective, machine learning approaches play a pivotal role in developing classifiers for a fast, reliable multiparametric biosensors output. Supervised model based on multivariate data processing has been undertaken to enable multiplexing, *i.e.* the simultaneous quantification of three biomarkers, namely MUC1 and CD55 proteins and KRAS DNA mutated sequence, in plasma and cysts' fluid samples. The main technological aspect of the SiMBiT device, with particular emphasis on the potency of machine learning approaches, will be discussed.

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DATA GEOMETRY TO SOLVE CLUSTERING AND UNMIXING ISSUES

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Clustering and spectral unmixing are common methodologies in hyperspectral image analysis. Clustering aims at partitioning similar pixels by looking at their spectral signatures, assuming that the spectrum of one pixel belongs to one cluster only. Linear spectral unmixing aims at identifying pure components under the assumption that a pixel is a linear combination of pure spectral profiles. However, in cases where the initial estimation of the number of clusters or components is tricky, or when spectra profiles are very similar, none of the approaches provides satisfactory results. We illustrate this issue by comparing the results of K-means for clustering and Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) for spectral unmixing analyses, applied on a complex Laser Induced Breakdown Spectroscopy (LIBS) hyperspectral image of a turquoise rock sample[1]. A geometric interpretation based on convexity of normalized scores and loadings data points, resulting from Singular Value Decomposition analysis (SVD), is proposed in this work, to extract the most useful (essential) information, in terms of linear mixture analysis, and to guide the interpretations of complex scenarios in which, the methods introduced previously cannot provide a comprehensive information[2,3]. Visualizing and understanding the structure of spectral data at hand is, indeed, a key step for selecting the appropriate analysis methodology, even more important when no a priori knowledge or ground truth information is available. This work opens the door to the development of new methods, in situations where the data structure deviates from the ideal one for clustering and spectral unmixing.

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O3-CH

A SURVEY OF DATA FUSION STRATEGIES WITH FOCUS ON ANALYTICAL APPLICATIONS

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The continuously increasing complexity of analytical problems to be tackled (e.g., in omics/systems biology, clinics or food quality) together with a wider availability of high throughput techniques result in samples being often characterized through multiple analytical platforms (sometimes even producing data of different orders, e.g., 1D profiles and 2D landscapes). Such a scenario, from a data analytical standpoint, represents an opportunity, since the integration of multiple data blocks into a single chemometric model can provide a deeper insight into the system under investigation, especially if the chosen instruments possess complementary features.

This communication will illustrate some of the most common protocols for data-fusion, highlighting their main characteristics, pros and cons[1]. Attention will be main focused on predictive models, but exploratory and curve resolution approaches will also be considered. Particular attention will be posed on the approaches able to extract common and unique information from the different blocks of data. Moreover, some recently proposed "out-of-the-box" applications, such as the possibility of fusing differently preprocessed data[2], will also be presented.

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O4-CH

DEVELOPMENT AND OPTIMIZATION OF UPLC-HRMS METHOD FOR METABOLOMIC CHARACTERIZATION OF MOUNTAIN DENOMINATION FOOD USING EXPERIMENTAL DESIGNS

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Ultra-performance liquid chromatography-high resolution mass spectrometry is one of the most widely used and powerful techniques for the determination of metabolites in food matrices[1,2]. However, the obtained chromatograms are often very complex in terms of dimensionality and subject to co-elution phenomena. It is therefore of paramount importance to optimise the analytical method to obtain resolved signals that can be more easily analysed. In this study, chromatographic conditions for the metabolomic analysis of food commodities with mountain denomination label were optimised by means experimental design techniques. In particular, a Central Composite Faced Design[3] was employed to investigate key chromatographic parameters: initial and final organic phase percentage, flow rate, time gradient, and length of an initial isocratic phase. The data obtained were analysed by means multivariate data analysis and the optimal conditions were determined based on the best resolution of chromatographic peaks corresponding to metabolites. Finally, the optimized methods were applied to different foods from mountain and plane regions in order to identify potential differences among samples according to their origin.

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Acknowledgements:

We would like to acknowledge Università degli Studi di Modena e Reggio Emilia for funding this research with the grant “FAR 2021 MO – Linea FOMO”.

O5-CH

FUSION OF DIFFERENT SPECTRAL FEATURES TO EXPLORE THE DISTINCTIVE SIGNATURES OF MOUNTAIN FOOD PRODUCTS

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The MOUNTAIN-ID research project focuses on developing analytical methodologies to support the identification, sustainability, and value of certain mountain products, including Parmigiano Reggiano cheese. Parmigiano Reggiano is a renowned Italian food product with a PDO (Protected Designation of Origin) label and a significant portion of its production taking place in mountain areas. The European Community has established a quality label called "Mountain Product" in a regulation specifically reserved for food products produced and processed in mountain areas. This label aims to support the economy in underprivileged areas by promoting and protecting the authenticity of these products[1]. However, the "Mountain Product" label is not yet well-known among consumers. In the present work related to the MOUNTAIN-ID project, the objective is to accurately detect and classify different Parmigiano Reggiano samples, specifically those characterized by the mountain denomination and additional requisites established by the producer consortium known as "Prodotto di Montagna - Progetto Territorio Consorzio" ("Quality Project - Mountain Product"). To achieve this goal, various spectroscopic techniques such as ^{1}H-NMR (proton nuclear magnetic resonance), NIR (near-infrared), MIR (mid-infrared) and Raman spectroscopy are employed. The use of chemometric tools like data fusion, variable selection, and classification techniques, aid in the development of robust analytical methodologies which accurately differentiate and classify Parmigiano Reggiano samples based on their mountain-specific characteristics and adherence to the "Mountain Product" requirements, ultimately increasing consumer awareness and appreciation for these high-quality food items.

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MULTIBLOCK METHODOLOGIES APPLIED TO MULTIOMICS DATASETS WITH CLINICAL AND DIAGNOSTIC OBJECTIVES

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Congenital heart disease (CHD) screening methods are still limited and not sensitive. This study was based on individuate metabo-lipidomics differences in a cohort of mothers with congenital heart disease in offspring (157 patients) compared to controls (162 patients) were analysed using ultra high-performance liquid chromatography (UHPLC) coupled to trapped ion mobility mass spectrometry (TIMS). Polar metabolome and Lipidome were separately analysed by two different strategies, namely HILIC and RP-UHPLC, in both ionization polarity ($ESI^{+/-}$). Each dataset and polarity were aligned, filtered and resulting features annotated against MS/MS spectral libraries. Therefore, we evaluated different chemometrics approaches to maximize information from omics platforms while minimizing variables and defining biological mechanisms. For biological purposes, a discrete number of molecules is needed to identify the correct metabolism, while for clinical and diagnostic goals, fewer identified molecules are desirable to reduce cost, analysis time, and accessibility. We compared classical approaches with multiblock algorithms.

The multivariate data analysis involved custom routines and standard Matlab functions in Matlab R2022b. Zeros were replaced with one-fifth of the minimum value for each molecule in the normalized dataset. The data was log-transformed, autoscaled, and subjected to Principal Component Analysis (PCA) for exploratory analysis. Partial Least Squares Discriminant Analysis (PLS-DA) was used to assess discrimination between classes, and Variable Importance in Projection (VIP) scores identified significant lipids. Sequential and Orthogonalized PLSDA (SO-PLSDA)[1] and Covariance Selection (SO-CovSel)[2] were applied for clinical variable selection.

The optimal SO-CovSel model obtained over 95% accuracy in cross-validation and 92% testing using five variables.

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O7-CH

A MULTI-OMIC APPROACH COUPLED TO CHEMOMETRICS TO IDENTIFY ILLICIT STORAGE TREATMENT IN FRESH FISH

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The identification of foods subjected to illicit conservation treatments applied to extend their shelf life, is fundamental in the field of food control of fresh products. Fresh fish products are particularly subjected to this type of fraud, due to the high commercial value of some fish species, and to the necessity to transport them over long distances. These treatments can involve the bleaching of the meat and / or the momentary abatement of the microbial load, while degradation continues, sometimes also producing molecules potentially dangerous to health. The development of methods allowing the identification of illicit treatments based on easy sampling procedures that can be applied in the field is therefore fundamental.

This study was performed on sea bass samples divided into four groups: controls stored on ice in the fridge for 3 h; controls stored under the same conditions for 24 h; treated with a solution of hydrogen peroxide and citric acid for 3 h; and treated with the same solution for 24 h (these last two groups, while they are kept on ice in the fridge). Different parts of each fish (eye, muscle, skin, gills) were sampled by the use of polymeric strips functionalized with adsorptive beads. The strips were then extracted with different media according to the final analysis: lipidomics and proteomics (muscle, skin) by UHPLC-HRMS and metabolomics (muscle, skin, eye, gills) by GCxGC-MS.

The collected data were processed using multivariate pattern recognition (PCA, cluster analysis) and classification (PLS-DA, SIMCA, Artificial neural networks), also coupled to variable selection procedures, to correctly identify the samples treated illegally from the control samples and identify biomarkers of the illicit treatment.

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Acknowledgements:
The work is financed by Ministero della salute (Ricerca Finalizzata 2016 - GR-2016-02363722 - The use of Led multi-spectral imaging for fast and innovative indexing of seafood preservation)

O8-CH

CHEMOMETRIC ANALYSIS FOR TRACEABILITY OF HIGH-VALUE ITALIAN RICE CULTIVARS: A MULTI-PLATFORM APPROACH

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Rice (*Oryza sativa* L.), with its long history of domestication and cultivation in China, remains a crucial dietary staple for a significant portion of the global population. Its nutritional composition (~75% of carbohydrates, 8% of protein, and ~2 % of fat, rich in essential minerals, vitamins, and phytochemicals) contributes to its widespread consumption and in ensuring food security worldwide[1]. Italy, the largest rice-producing country in Europe, boasts a remarkable variability of cultivars and biodiversity. In this context, this study seeks to preserve the authenticity and integrity of high-value commercial varieties by supporting the development of tracing technologies for Protected Geographical Indication (IGP) and Protected Designation of Origin (DOP) Italian rice cultivars. Several DOP varieties from Baraggia (Carnaroli, S. Andrea, and Arborio) were collected directly from different producers. Additionally, the Carnaroli variety was sampled from various Italian production areas, including Piana di Sibari (CS), Valle Lomellina (PV), Roseto degli Abruzzi (TE), and the Carnaroli IGP rice "Delta del Po". These samples were extensively characterized using three different analytical techniques. ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) was employed to obtain a mineral fingerprint of the cultivars and their geographical origin, obtaining satisfactory results through a technique that shows high sensitivity but is expensive and requires appropriate sample pretreatment. ATR-FT-IR (Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy) was used to acquire mid-infrared spectroscopic profiles rapidly in a non-destructive manner. Multivariate Image Analysis was employed to process data collected by an RS Pro portable microscope, aiming to develop a fast, easy, and routine-compatible method for rice quality control. Chemometric analysis, conducted separately on the different datasets, enabled the comparison of the techniques in terms of reliability, efficiency, and versatility for traceability purposes. ASCA (Anova- Simultaneous Component Analysis) was employed to explore the data and confirm the significant effects of cultivar and producer (production area) for the DOP "Baraggia Biellese and Vercellese" sites, whose production must comply with strict DOP specifications. PLS-DA (Partial Least Squares-Discriminant Analysis) was applied to achieve geographical discrimination, specifically for the Carnaroli variety. Finally, SIMCA (Soft Independent Modeling of Class Analogy) was employed to authenticate the Carnaroli IGP and DOP cultivars.

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O9-CH

STUDY OF THE SOURCES OF VARIANCE IN MINIATURIZED NIR SPECTROSCOPY THROUGH ANOVA-SIMULTANEUOUS COMPONENT ANALYSIS (ASCA)

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ASCA (ANOVA–Simultaneous Component Analysis)[1] is a multivariate data analysis technique that combines the principles of Analysis of Variance (ANOVA) and Principal Component Analysis (PCA). It is specifically designed for the analysis of complex experimental designs, where multiple factors are simultaneously investigated, and the datasets are high-dimensional. It aims to identify the main effects of factors, interactions between factors, and how they relate to the underlying sources of variation in the data. This study proposes the use of this effective tool to detect and comprehend the influences of the different factors on the raw and preprocessed spectroscopic signal for the first time in our knowledge[2]. Specifically, the research focus on signals recorded by miniaturized NIR sensors.

The literature has provided evidence of the efficacy of miniaturized NIR devices across various applications[3]. The idea of small portable instrumentation that could be used directly in the field and/or online suitably fit into the logic of process analytical technologies and green analytical chemistry. Alongside the successful outcomes, only a few studies systematically investigate the sources of variability of this technique[4].

This study analysed different types of solid samples of worldwide interest with five miniaturized spectrometers. Differences in package forms and compactness, sample colours and chemistry were considered. The comparison of various portable sensors was interesting since the results could significantly vary in the same application, justifying the idea that this kind of spectrometers is not to be treated as a general class of instruments.

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O10-CH

AN ANALYTICAL STRATEGY BASED ON HSI-NIR AND CHEMOMETRICS FOR THE NON-CONTACT QUANTIFICATION OF COLLAGEN IN BONES.

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Many rarest bones and human remains in Prehistory are much too precious and considered a cultural and historical patrimony, and so the application of destructive methods -such as 14C- must be as limited as possible. The identification and quantification of collagen in archaeological bones play a crucial role in the 14C dating protocol because a significant amount of proteins (1% yield of collagen) [1] is requested for performing a reliable radiocarbon analysis. The advantages of the HSI-NIR technology can be of high impact in this context, in particular regarding the non-destructiveness and the possibility to map, from a spatial extent, the area of the bone in which the proteins are more present. A first milestone in mapping collagen in bones by means of HSI-NIR was achieved by the authors [2], applying the NDI approach to few archaeological samples. Acting upon this, a quantification model is now proposed thanks to the analysis of 60 archaeological bones, ranging back from the modern age to more than 50,000 years ago. For the development of the PLS regression model, NIR images of both bone powders and fragments were acquired in the spectra range 1000-2500 nm (Specim SWIR 3 camera) and then the samples were submitted to collagen extraction at the BRAVHO 14C lab, following the procedures of Talamo et al. 2021[1]. With a RMSECV of 2.2% wt, the proposed strategy was applied to unknown samples demonstrating how HSI-NIR can be a sustainable pre-screening method to quantify the presence of collagen on bone samples in a non-destructive way.

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Financial support provided 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.

THE ROLE OF CHEMOMETRIC STRATEGIES IN PROCESSING MULTIBLOCK HYPERSPECTRAL DATA FOR THE SELECTIVE IDENTIFICATION OF BIOLOGICAL FLUIDS IN FORENSIC EVIDENCE

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Nowadays, the development of new techniques and method allowing to detect and identify minute forensic biological traces in a selective and non-destructive way is an urgent research issue. Indeed, traditional methods used for identifying these fluids, such as blood, semen, urine, and saliva, have limitations due to the complex and heterogeneous sample matrices in which they are often found, as well as degradation effects that may occur over time.

The present study delineates the application of a novel multiblock platform (IRIS, XGLab SRL – Bruker Nano Analytics) that simultaneously acquires X-ray fluorescence (XRF, 1-40 keV) data together with visible & near-infrared (VNIR, 380–1100 nm) and short-wave infrared reflectance spectra (SWIR, 1100–2500 nm), coupled with chemometric methods to localize and identify dehydrated biological fluids.

To exploit the complementary information embedded in the different hyperspectral data blocks and to identify the different components in each sample, an efficient multivariate strategy based on principal component analysis (PCA) and multivariate curve resolution alternating least squares (MCR-ALS) was applied. The chemometric strategy proved to be highly efficient in the analysis of 3D data arrays by resolving overlapped vibrational bands and correlating elemental information.

The performances of the chemometric strategy were evaluated for the differentiation of different biological fluids on wood and cotton tissue, producing multivariate chemical distribution maps, with and without the exploitation of reference spectra of pure components.

Acknowledgements:
IRIS is an analytical instrument developed in the framework of the project "MOBARTECH", co-financed by Regione Lombardia (POR FESR 2014 – 2020)

O12-CH

A NON-TARGETED APPROACH BASED ON RAMAN SPECTROSCOPY AND CHEMOMETRICS TO STUDY APULIAN AND SICILIAN TOMATOES FROM ORGANIC AND CONVENTIONAL FARMING

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In recent years, the consumption of organic food has increased dramatically. That growth is related to several reasons: the fact that consumers expect improved nutritional values from them compared to conventional products, and to the issues related to sustainability[1].

In addition, the lack of chemical markers capable of discriminating agricultural products between organic and conventional makes the market susceptible to fraud in products labeled as "organics"[2].

This work aims to describe an analytical method, based on Raman spectroscopy and chemometrics, with an encouraging potential in discriminating organic from conventional tomatoes.

This procedure consists of the acquisition of Raman spectra directly on the external surface of the sample, without any pretreatment, and on the subsequent application of chemometric methods of exploration and classification on the data matrix.

A Principal Component Analysis (PCA) was performed on the data matrix consisting of 220 spectra of Apulian and Sicilian tomatoes from organic and conventional farming. The exploratory analysis shows a trend in the separation of samples by production methods and which are the characterizing variables.

Moreover, a robust classification model was built by Partial Least Square Discriminant Analysis (PLS-DA), which confirmed the ability to classify samples as organic or conventional based on the Raman spectrum.

The presented method could be used in quality control to classify samples through a sensitive, fast, low-cost and non-destructive method.

Thus able to be used as a screening procedure for verifying the information declared in the label, and to assess the traceability and authenticity of the product.

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Oral Spettroscopia

O1-S

THE IMPORTANCE OF ANALYTICAL SPECTROSCOPY IN THE FASHION INDUSTRY

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The interest in scientific research within the metal finishing sector is growing. The demand for durable metals and adaptable manufacturing processes is increasing across a wide range of applications, from aerospace and automotive to machinery and jewelry. In that respect, alloy plating offers better answers in terms of economic growth and environmental sustainability due to fine-tuning composition, morphology, and crystallinity[1]. Here, current trends in alloy electrodeposition research are reviewed highlighting open challenges and process innovations from an industrial perspective. Combining basic electrochemical techniques with spectroscopic, microscopic, and structural techniques is crucial for characterizing the structure-activity relationship for many different technological devices. Particular attention is devoted to advances in industrial quality control by Analytical Spectroscopy[2] for the reduction of precious metal content in electroplated accessories as well as the replacement of cyanide and nickel baths with non-toxic compounds.

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O2-S

ASSESSING INTERMETALLIC DIFFUSION IN ELECTROPLATED GOLD COATINGS: A COMBINED EDS AND XRF SPECTROSCOPIC APPROACH

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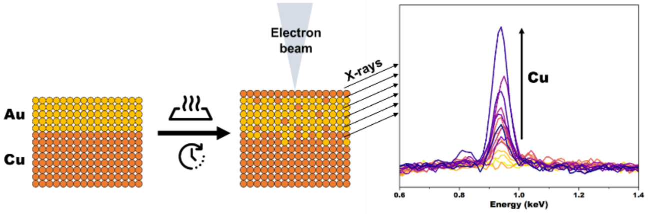
Intermetallic diffusion is crucial in metallurgical processes like electroplating, where a metal layer is deposited onto a substrate. It can result in intermetallic compound formation, influencing coating properties. Accurate determination of metal diffusion coefficients is vital for functional and decorative coatings. In this research, a copper substrate was electroplated with a thin layer of gold, and subsequent XRF and EDS analyses were conducted to measure the gold coating thickness and the amount of copper diffused into it, by means of Monte Carlo standardless quantification[1]. By employing Fick's law, an equation was derived to calculate the diffusion coefficient[2]. The gold layer's thickness was chosen to mimic applications in functional and decorative coatings (<1 μm). The samples were subjected to temperatures ranging from 100°C to 200°C for durations of 12 to 96 hours. A linear relationship between the logarithm of the diffusion coefficient and the inverse of the temperature was verified, consistent with literature values. The obtained diffusion coefficient values ranged from 10^{-19} to 10^{-14} cm^2/s within the considered temperature range, aligning with existing literature reports.

The results of this study present a simple, alternative, and quantitative method for determining diffusion rates, holding potential applications in electroplating and other metallurgical processes. This approach paves the way for designing and implementing procedures to create barrier layers that prevent undesirable diffusion.



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Acknowledgements:

Progetto "3A-ITALY - Made-in-Italy circolare e sostenibile" con codice PE_00000004 (CUP B83C22004890007) finanziato da PNRR (M. 4, C. 2, I. 1.3) del MUR.

O3-S

XPS ANALYSIS OF BUFFER AND CONCENTRATION EFFECTS ON DOPAMINE POLYMERIZATION FOR ONE-HEALTH APPLICATIONS

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Polydopamine is a versatile polymer that can bind different functional groups, making it valuable in many applications. It has emerged as a multifunctional material with remarkable properties and multiple scientific and technological uses[1]. Dopamine easily polymerizes in alkaline aqueous solutions, forming polydopamine (PDA), a robust underwater adhesive polymer[2].This study focused on the spontaneous polymerization of dopamine in slightly alkaline buffered solution to form PDAfilms. To investigate the influence of different buffers and concentrations on the dopamine polymerization process, X-ray photoelectron spectroscopy (XPS) was employed. XPS is a sophisticated technique that allows for the analysis of the functional groups involved in surface reactivity, providing valuable insights into the chemical composition and bonding states of the surface species[3]. The results showed that dopamine polymerization varied depending on the specific buffer and dopamine concentration used. Finally, the study proposes functionalizing PDA for biosensing to detect bacteria like *Listeria monocytogenes*, enabling rapid and accurate identification for applications in food safety and clinical diagnostics.[4]

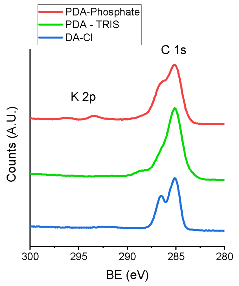

Figure 1: XPS analysis of three surfaces

Acknowledgements:
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O4-S

XPS CHARACTERIZATION OF QDs-TiO_2 NANOCOMPOSITES FOR SOLAR FUELS PRODUCTION

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TiO_2 is one of the most applied photocatalyst due to its great efficiency, cost effectiveness and low toxicity, but TiO_2 is not able to absorb visible and NIR photons. Due to their exceptional optoelectronic properties, colloidal quantum dots (QDs) can be applied either as sensitizer or as photocatalyst. NIR emitting $CuInS_2$ (CIS QDs) have been chosen as sensitizer for diverse types of TiO_2 substrates. In this study, we present the investigation by XPS of TiO_2 polymorphs decorated with heavy-metal-free quantum dots (QDs) for solar fuels production. The surface chemical composition and speciation of nanocomposites loaded with different CIS QDs amounts have been correlated with their performance in the photocatalytic conversion of CO_2 under simulated sunlight (i.e., 100 mW/cm^2 of intensity). The nanocomposites structure and properties have been also investigated by means of x-ray powder diffraction (XRPD), UV−Vis spectroscopy, N_2 adsorption/desorption at −196 °C, electrophoretic mobility (ζ-potential), FT-IR measurements, and electron microscopy (TEM/SEM). Preliminary results on the different functioning based on the TiO_2 polymorphic type and QDs loading will be presented.

O5-S

AN ANALYTICAL APPROACH FOR CLARIFYING THE ZINC IMMOBILIZATION BY MARBLE WASTE POWDERS.

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Marble waste powders (classified under Italian regulations as special waste) from a Sardinian quarry in Orosei were proved to be an effective sorbent for lead and manganese removal from polluted water[1,2]. Their use as sorbent for water remediation is in line with the European Union Circular Economy Strategy.

In this work the removal efficiency toward zinc is presented. Proper amount of marble powder was suspended in model solutions of zinc nitrate ranging from 0.4 mg/dm^3 to 100 mg/dm^3. The influence of zinc concentration, temperature, and contact time on the zinc removal have been investigated.

Solution analyses by ICP-OES provide the evidence of marble waste effectiveness in zinc removal: when the initial concentration of zinc is lower than 50 mg/dm^3. The concentration of residual zinc is below the legal limit for surface water (0.5 mg/dm^3, see Figure 1a)

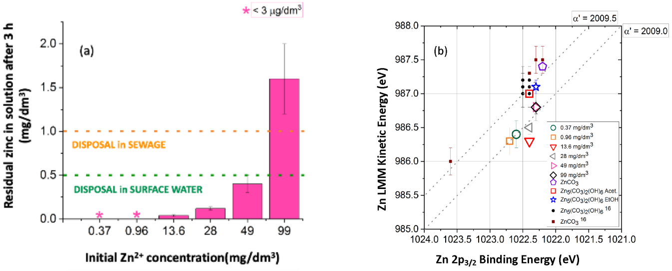

Figure 1: a) Residual Zn^{2+} in solution after the contact with marble waste. b) Zinc chemical state plot

Zinc speciation can be achieved combining data from XPS and XAES spectroscopies in the chemical state plot (Figure 1b). The chemical state of zinc on the surface of marble powder is different from standards ($ZnCO_3$, $Zn_5(CO_3)_2(OH)_6$), thus a simple precipitation of a zinc compound, e.g. hydrozincite, as removal mechanism can be ruled out. Instead, following the contact of marble waste powder and zinc solution, the formation of a mixed Ca/Zn carbonate phase is proposed.

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Acknowledgements:

University of Cagliari (UniCA) and Fondazione di Sardegna (FdS) are gratefully acknowledged for the financial support – Project number CUP F73C22001190007 (2021): “Sorbents for environmental applications: a synergetic computational modelling and experimental approach.”.

Progetto finanziato dall’Unione Europea - NextGenerationEU – Piano Nazionale di Ripresa e Resilienza (PNRR) - Missione 4 Componente 2 Investimento 1.3 – Avviso N. 341 del 15.03.2022 del Ministero dell’Università e della Ricerca (MUR); Award Number: codice progetto PE0000021, decreto di concessione del finanziamento n. 1561 dell’11.10.2022, titolo progetto “Network 4 Energy Sustainable Transition – NEST”

O6-S

XPS AND ATR FTIR INVESTIGATION OF FUNCTIONALISED POLYMER SURFACE

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In order to prevent the proliferation of bacteria that compromises the shelf-life of food products, the interest toward the development of new food-packaging materials with antimicrobial activity is growing. One route to obtain antimicrobial food-packaging is the surface functionalization of commercially available food-grade polymer[1] with antimicrobial active agents. This work focuses on the optimization of food-grade polyvinyl chloride (PVC) functionalization with an antimicrobial active polymer, the polyhexametilenguanidine (PHMG). Food-grade PVC functionalization was first carried out following a literature procedure [2] for medical-grade PVC then, the synthesis was modified with a bottom-up approach as described in the following. Food-grade PVC functionalized with PHMG was obtained immersing 1 cm^2 as received PVC in a 10% ethanol solution of (3-mercaptopropyl) trimethoxysilane (MPTMS) for 1 h, followed by the grafting of (APTES), 1% glutaraldehyde, and finally with PHMG. All steps were characterized by means of ATR FTIR spectroscopy, in order to confirm the functionalization by the assignment of the characteristic absorption of the Si-O, -NH_2, and S-C bands. The ATR FTIR results confirmed the correct surface functionalization and are in good agreement with the literature. Moreover, it was possible to fully characterize the first step by means of X-ray photoelectron spectroscopy (XPS) and angle-resolved XPS that allows us not only to provide evidence of the formation of a self-assembled monolayer of MPTMS onto the polymer surface but also to assess the surface homogeneity and the determination of its composition. The results suggest the formation of a lateral homogeneous self-assembled monolayer and the ratio of Si:S:O was found equal to 1:1:2.5 in good agreement with the stoichiometry. The relative depth-plot shows that the -OCH_3 groups are oriented towards the outer part of the layer, followed by O-Si-O while S is located at the interface MPTMS-PVC. Furthermore, the film thickness calculated from the ARXPS results resulted to be 2.2 ± 0.2 nm[3], which includes the contamination layer.

The antimicrobial activity tests towards strains of bacteria as *Escherichia coli* and *Staphylococcus aureus* at different contact ratio are ongoing and will be discussed together with SEM micrographs and the XPS results of all functionalization steps.

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Acknowledgements:

The authors are grateful to: MIUR- Fondo per lo Sviluppo e la Coesione FSC-Piano Stralcio 2015/2017 for the Ph.D. grant assigned to Giulio Casula (Consortium UniCa and UniSS); – Project number CUP J89J20000930001 (2021): "Functionalization of Food Packaging with active antimicrobial agent" and to the University of Cagliari (UniCA) and Fondazione di Sardegna (FdS) for the financial support UNICA-FdS (Fondazione di Sardegna) 2019 – Project number CUP F72F20000240007

O7-S

PLASMONIC SENSOR FOR DETECTING CIRCULATING BIOMARKERS

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To advance the usefulness of plasmonic sensors based on Surface Plasmon Resonance Imaging (SPRI) in the field of personalized diagnostics, we need to have an ultimate device able to detect the biomarker or analyte of interest (i.e., tumor DNAs, cell-free DNA, proteins, and microRNAs) circulating at ultralow concentration in a complex biological matrix, such as serum or plasma, with high selectivity. Here, we will present the challenges and opportunities of our sensing device to achieve low concentration sensitivity in the attomolar range, by adopting an appropriate sensor design relying on functionalized gold nanoparticles, peptide nucleic acid probes (PNA) and antifouling strategies[1]. By implementing a simplified liquid biopsy approach, ~1 aM circulating KRAS mutated DNA was revealed directly in 40 µL of plasma from cancer patients[2]. A similar approach was also applied for non-invasive prenatal fetal sex determination by detecting a Y-chromosome specific sequence (single-gene SRY) in cell-free fetal DNA from maternal plasma, even at the earliest gestational age[3]. A new anti-fouling PEG-pentrimer carboxybetaine-modified surface has proven its applicability for the SPRI biosensing of human Arginase in plasma[4]. Possibilities offered in the quantification of microRNAs[5] as cancer biomarkers circulating in the serum of glioma patients will be also discussed. The development of enhanced performance based on this platform opens the way for multiplexing, non-invasive, and cost-effective diagnostic tools.

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Acknowledgements:

We acknowledge support from the European Union's Horizon 2020 research and innovation programme under grant agreement No 633937 project ULTRAPLACAD, from the European Union's European Innovation Council under grant agreement No 101046217 project VERSILIB and from Università degli Studi di Catania, STARTING GRANT 2020, project PATmiREC.

SPECTROSCOPIC AND MORPHOLOGICAL CHARACTERIZATION OF GREEN-SYNTHESIZED COPPER NANOPARTICLES FOR ANTIMICROBIAL APPLICATIONS.

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Analytical spectroscopy is fundamental in nanoantimicrobials (NAMs) characterization. An exhaustive analysis and the appropriate choice of methodologies for nano-toxicological risk assessment promise nowadays a reliable data output to guarantee NAMs safe application in real-life products. In this communication, analytical spectroscopy was used to guide and support the production of human-safe copper nanoparticles (CuNPs). Cu is an essential component of many enzymes and also possesses good antimicrobial activity[1]. This study demonstrates a simple approach to synthesize green core-shell CuNPs stabilized by poly(n-vinyl)pyrrolidone (PVP). CuNPs were prepared using copper sulfate as precursor and glucose as reducing agent. The synthesis of small CuNPs employing glucose as reductant is known since 2006[2], but the whole process was carried out in nitrogen atmosphere to prevent CuNP oxidation. The presence of PVP in the synthetic medium eliminates the need for an inert atmosphere[3]. PVP can act as stabilizer, dispersant, and reducing agent, its role depending on synthetic conditions. This is possible thanks to the amphiphilic nature of PVP, along with its stabilizing capability. The influence of glucose and PVP concentrations, along with pH of the synthetic medium, were here investigated, considering colloidal stability and NP average size as discriminating issues. Synthetic parameters were properly tuned to obtain NPs with diameters above 100 nm. This way, the dangerous nano-cytotoxicity associated to the use of smaller NPs was waived *a priori*. A thoughtful spectroscopic characterization of CuNPs was performed by infrared, UV-Vis and X-ray photoelectron spectroscopies. These measurements demonstrated the formation of a PVP layer around a Cu(0) core. Size distributions and average shell thickness were obtained by statistical analysis on transmission electron microscopy micrographs. Cu@PVP particles were embedded in polymer matrices to prepare coatings for food packaging. Cu^{2+} release kinetic was assessed by atomic absorption spectroscopy, and used to theorize the antimicrobial potential of the composites. The coatings showed a controlled release of Cu^{2+}, which maximum laid below the WHO regulatory limits (25 ppm)[4]. These coatings represent promising candidates for the preparation of bioactive food packaging, with negligible cytotoxicity associated to their use.

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Acknowledgements

Authors acknowledge the Project "Imballaggio Attivo Ortofrutticoli", Grant n° J98H23000070008, from the "Ministero dell'Agricoltura, della Sovranità Alimentare e delle Foreste" for the finantial support to this research.

O9-S

PLGA MICELLE-STABILIZED ANTIMICROBIAL CERIUM OXIDE NANOPARTICLES INCORPORATION IN GELATINE AND MAIZE STARCH FILMS

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In the last years, cerium oxide nanoparticles (CeO_2NPs) have caught the attention in research world related to biomedical field. Particularly, antimicrobial and antibiofilm activity is being investigated[1]. In this work, a new system based on CeO_2NPs protected in a polymeric matrix formed by PLGA micelles was developed, to avoid the rapid oxidation of cerium oxide. The synthesis of CeO_2NPs was carried out following the W/O microemulsion method[2]. Subsequently CeO_2NPs were encapsulated in PLGA micelles. Encapsulation in micelles was performed according to the single emulsion/solvent method. All formulations (free NPs, empty micelles and loaded micelles) were incorporated in two types of films for food packaging use, according to solvent casting method, equilibrating the right ratio between gelatine or starch and glycerol. The main components of these films were gelatine or maize starch, both in different ratio with glycerol. The chemical and physical characterization of the NPs and micelles solutions was carried out by Dynamic Light Scattering (DLS), to determine the size and zeta-potentials, Transmission Electron Microscopy (TEM), and X-ray Photoelectron Spectroscopy (XPS). The interactions among the film matrix compounds and the incorporated colloids (micelles and NPs) were investigated by Scanning Electron Microscopy (SEM) and XPS: blank films were compared with films incorporating micelles and NPs[3,4].

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O10-S

PROBING THE INTERACTION BETWEEN NANOANTIMICROBIALS AND LIPID MEMBRANES

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Metal-based nanoparticles (MeNPs) have been demonstrated to provide effective antimicrobial functionality in different technological fields, including the food packaging industry. However, their size, chemical composition and enhanced reactivity can induce undesired interactions with biological systems, rising significant nanotoxicology concerns[1]. The first step in investigating the toxicity mechanisms of nanoantimicrobials is the exploration of permeability and distribution of NPs in cell membranes. To this end, lipid nanoparticles, also known as liposomes, can provide a simplified, repeatable and robust experimental model for such purpose. In this context, this contribution presents an analytical chemistry holistic approach for the assessment of the interactions between different antimicrobial MeNPs (e.g. AgCl NPs, CuNPs, AgNPs) and phospholipid membranes, based on fluorescence spectroscopic investigation. Large unilamellar vesicles (LUVs) made of soybean phosphatidylcholine, with an average diameter of 100 nm, were used as biomimetic eukaryotic cell membranes. The individual incorporation of two fluorescent membrane probes bearing naphthalene moieties (namely, Laurdan and Prodan) was used to investigate the interactions with the biomembranes[2,3]. In particular, such probes are able to penetrate into the phospholipid bilayer at different depths. Their fluorescent properties, which depend on the polarity of the microenvironment they are surrounded by, allow low resolution monitoring of changes in bilayer organization by generalized polarization (GP) measurements, providing specific information about alterations in lipid order, packing and hence membrane hydration and permeability. The results demonstrated a fluorescence hypsochromic shift, which is attributed to the progressive membrane dehydration at the hydrophobic-hydrophilic interface region of the membrane in which the probe's fluorophore is aligned. Furthermore, such results suggested an enhancement of lipid packing in the presence of MeNPs.

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O11-S

CHARGE TRANSFER ESTIMATION IN MOLECULAR CRYSTAL THROUGH RAMAN AND INFRARED SPECTROSCOPIES: A THEORETICAL STUDY

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Analytical spectroscopy techniques such as Raman and IR are often employed to characterize binary π-complex molecular crystals (MC) and estimate their charge transfer (CT). These systems are of interest to the sensor and semiconductor industries because their properties, like optical bandgap, can be tuned by varying stoichiometry, crystalline structure, or substituents. CT based sensors are widespread in the medical field as markers for Alzheimer's disease[1] and to monitor metallic ions in physiologic processes[2]. CT is measured by the shift of sensitive modes from monomers to MC in Raman and IR spectra. Perylene-TCNQ (Tetracyanoquinodimethane) co-crystals and their fluorinated derivatives are among the most studied CT-MC as a prototypical system; this is because the CT varies in function of the degree of fluorination and crystalline structure. In literature CTs of Perylene-TCNQF$_x$ species are reported but those are frequently divergent[3]. The present study aims to develop a computational protocol to complement analytical spectroscopy for improving CT measurements and justify experimental data. α-Perylene-TCNQ (1:1) and Perylene-TCNQF$_4$ (1:1) were investigated because they have the lowest and the highest CT among the whole series; in addition, previous studies[4] on α-Perylene-TCNQ (1:1) report CT values varying from 0 to 0.2 e$^-$. Experimental structures from XRD data were optimized at the PBE/PAW level of theory using VASP; Vibrational density of states and band-structure calculations were subsequently performed. Theoretical IR and Raman spectra were calculated at PBE/PAW level, while CT was evaluated through different population analyses (Mulliken, Bader, DDEC6) both employing PAW and AO (atomic orbitals). AO calculations were performed on extracted dimers of the optimized structure at X/cc-pVTZ level where X=BLYP, B3LYP, CAM-B3LYP, PBE and PBE0. CT calculated employing DDEC6 population analysis has turned out to be not method dependent, providing the best results, in agreement with the literature and removing the ambiguity for CT of α-Perylene-TCNQ (1:1).

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Acknowledgements:

The authors acknowledge for the support offered by Fondazione CR Firenze, Fondazione per la Ricerca e l'Innovazione dell'Università degli Studi di Firenze and Confindustria Firenze within the FABER4 project.

O12-S

INSIGHTS IN THE ELECTROSYNTHESIS OF ZINC/CALCIUM HYDROXIDES: A SPECTROSCOPIC STUDY

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In this contribution, we report the electrochemical synthesis and the spectroscopic investigation of zinc/calcium mixed hydroxides nanostructures (NSs). The proposed strategy combines the sacrificial anode electrolysis of a zinc anode[1] and a precipitation method for $Ca(OH)_2$[2] in one-step, as an eco-friendly route to hybrid nanomaterials. This strategy is therefore advantageous as compared to previous works reporting the preparation of nanocomposites either by mixing nanomaterials prepared separately or by using a combination of preformed commercial nanoparticles. NaOH aqueous solutions have been used as electrolytic media. The role of temperature, strong base and calcium precursor concentrations, and pH has been studied by a detailed analytical characterization. In particular, TEM analysis provided the morphological information about the as-synthesized nanomaterials, whereas FTIR and XPS allowed investigating both their bulk and surface chemical composition. The development of hybrid systems with multiple properties is particularly appealing in the field of stone artwork preservation[3] as well as for other applications such antimicrobial/antiviral agents[4]. Therefore, we applied the hybrid NSs to prepare coatings that were then characterized in terms of contact angle measurements, Zn^{2+} ion release as well as their antimicrobial activity[5].

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O1-MS

Oral Spettrometria di massa

O1-MS

EXPLORING THE POTENTIAL OF EXTRACTIVE-LIQUID SAMPLING ELECTRON IONIZATION MASS SPECTROMETRY (E-LEI-MS) SYSTEM IN FOOD AND BIOLOGICAL APPLICATIONS

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Extractive-liquid sampling electron ionization-mass spectrometry (E-LEI-MS) is an innovative approach for coupling ambient sampling with electron ionization (EI), minimizing the sample preparation step, and providing identification based on the comparison between the experimental spectra with those of the National Institute of Standards and Technology (NIST) library[1].The E-LEI-MS configuration includes the vaporization microchannel (VMC), a capillary crossing the transfer line, kept at high temperature, where the analytes are released from the inlet capillary (40 μm i.d., 375 μm o.d.) and vaporized before reaching the EI source. In the VMC, analytes are vaporized at a high temperature and quickly pulled into the MS by the fast vacuum pump aspiration. The VMC avoids the potential occlusion of the inlet capillary caused by the early solvent evaporation near the ion source. The system was coupled to a triple quadrupole mass spectrometer to enhance sensitivity by operating in multiple reaction monitoring (MRM) acquisition mode. The E-LEI-MS was successfully applied in targeted and untargeted applications. A targeted biological application refers to pyochelin determination in bacterial colonies. Pyochelin is a siderophore produced by *Pseudomonas Aeruginosae*. Pyochelin detection by E-LEI-MS allows the rapid identification of bacterial colonies in clinical practice, providing a fast diagnosis. Another targeted application is focused on chlorpyrifos determination, a pesticide widely used in *Citrus* crops. The system, operating in MRM acquisition mode, allowed a semi-quantitative approach by plotting a calibration curve from orange peels fortified with solutions at increasing chlorpyrifos concentrations. Untargeted analysis regards the determination of bioactive compounds in herbal infusions. α-tocopherol acetate was identified with a satisfactory spectral match by Agilent Mass Hunter Unknows analysis software, proving the system ability to identify quickly unknown compounds despite the complexity of the sample analyzed.

E-LEI-MS demonstrated great potential as a promising, rapid, and green technique for direct analysis.

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Acknowledgment:

The authors are grateful to Agilent Technologies for providing the MS instrumentation.

INNOVATIVE APPROACHES FOR IMPURITY IDENTIFICATION: LIQUID ELECTRON IONIZATION INTERFACE COUPLED WITH HIGH- RESOLUTION MASS SPECTROMETRY AND NORMAL/REVERSED PHASE UHPLC

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High-resolution mass spectrometry (HRMS) coupled with HPLC/UHPLC, in combination with chemical databases, provides a powerful tool for modern non-targeted analysis[1]. Liquid electron ionization (LEI) is an LC-MS interface that converts a liquid phase to a gas phase allowing to couple liquid chromatography (LC) with electron ionization (EI) and chemical ionization (CI) in a high-vacuum environment. LEI is compatible with any mobile phase composition allowing it to switch from reversed to normal phase for different separation needs. The system advantages rely on the ionization of the analytes under EI conditions generating library searchable spectra with strong matrix effects mitigation, even in complex samples, and on the possibility to use softer ionization techniques that provide molecular ions, such as CI, for unknown compounds with ambiguous fragment spectra [2,3]. In this work, LEI was coupled with a time-of-flight quadrupole mass spectrometer (Q-TOF) for non-targeted analyses in complex matrices. Agilent Mass Hunter Unknown Analysis software was used for spectra deconvolution of coeluted compounds, allowing operational conditions optimization to achieve their separation. We used both EI at different electron energies (70 eV, 15 eV, and 9 eV) and CI in positive mode to provide the molecular ions. HR-MS/MS analyses were performed to determine the molecular structures, using each molecular ion as a precursor ion. The accurate mass MS/MS fragment ions obtained were compared with databases, such as PubChem and ChemSpider, using Agilent MassHunter Molecular Structure Correlator software. Preliminary MS/MS results showed high match scores with the candidate structures, ranging from 82.0 and 96.0, and dMs (theoretical mass and experimental mass difference) ranged from -2.2 and 5.0 ppm were obtained for the exact mass of each fragment, in line with the Q-TOF accuracy.

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A SIMPLE DILUTION AND SHOOT: LOW-PRESSURE GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY FOR THE DETERMINATION OF PHTHALATES IN EXTRAVIRGIN OLIVE OIL

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The object of the present research was to simplify the analytical workflow for the analysis of phthalates in olive oil through simple dilute and injection on low-pressure gas chromatography system.
Separation was achieved in 10 min through the use of low-pressure gas chromatography, followed by multiple reaction monitoring MS detection. The use of a relatively short (5 m) wide bore (0.53 mm I.D.) non-polar column allowed high sample capacity and fast analysis. While sensibility and selectivity were guaranteed using triple quadrupole mass spectrometry.
The limits of quantification were in the range 0.06-1.14 mg kg^{-1}. The accuracy was measured in term of percentage deviation, within repeatability conditions after 150 total analyses (-7.2 and 11.8%), and within intermediate precision conditions after further 80 analysis (-8.7 and 12.1%). At the end the method trueness was evaluated performing blind accuracy analyses. In this case the accuracy values were in a range of 88.4-114.2% between the experimental and the expected values.
Precision studies were conducted for the evaluation of the method in terms of intra-day and inter-day and were in a range of 0.2-11.2% and 3.5-11.7% respectively.

Acknowledgements:
The authors gratefully acknowledge the Shimadzu Corporation and Merck Life Science for their continuous support.

O4-MS

ON-LINE LIQUID-GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY FOR POLYCYCLIC AROMATIC HYDROCARBONS ANALYSIS IN EXTRA-VIRGIN OLIVE OIL

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The aim of this study was the development of a fully automatized liquid-gas chromatography method, with reduced solvents consumption, for a selective detection and quantification of the 16 European Union-priority polycyclic aromatic hydrocarbons in extra-virgin olive oil samples, full-filling the recent trends of green and sustainable analytical methods. An LC silica column, to retain the bulk of the matrix (mainly triglycerides), was employed, coupled to a gas chromatograph equipped with a triple quadrupole mass spectrometer, thus exploiting the greater selectivity of the tandem MS technique. Particularly, the pseudo-multiple reaction monitoring acquisition mode was employed to increase method selectivity.

The limit of detection and quantification values successfully satisfy the maximum level of 2.0 μg kg^{-1} for benzo[*a*]pyrene (BaP) and 10.0 μg kg^{-1} for the sum of BaP, benz[*a*]anthracene, benzo[*b*]fluoranthene, and chrysene, defined by the European Legislation in 2011. The accuracy values (at 2 and 20 μg kg^{-1} concentration levels) were in the 86.9-109.3% range. The intra-day and inter-day precision values were in the 1.2-10.8 and 3.2-12.8 ranges, respectively. For all the investigated analytes, a negative matrix effect was observed.

Acknowledgements:

The authors gratefully acknowledge the Shimadzu Corporation and Merck Life Science for their continuous support.

DEVELOPMENT OF A MASS-SPECTROMETRY-BASED APPROACH FOR THE EVALUATION OF THE MIGRATION OF ALLERGENIC PROTEINS FROM PLANT-BASED FOOD CONTACT MATERIALS

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The production of bio- and plant-based food contact materials (FCMs) raises new food safety issues related to the possible migration of intentionally and non-intentionally added substance into foods. The aim of the present work was to develop an analytical strategy to get insights into the release of allergenic proteins from these materials to food products, which is a completely unexplored food safety risk so far[1].
First, model materials were prepared using lupin flour, a recognized allergenic ingredient in which conglutins are the major allergens, and chitosan, which serves as binder; the dough was shaped into sticks and dried. The migration experiments were performed by dipping the sticks for 1h at room temperature into acetic acid 3% (*w/v*) or ethanol 20% (*v/v*), which simulate acidic and alcoholic foods and beverages, respectively (EU Regulation N. 10/2011). After migration, the simulant was submitted to a bottom-up proteomic workflow based on tryptic digestion, pre-concentration, and liquid chromatography/tandem mass spectrometry (LC-MS/MS) analysis with a linear ion trap. Unique tryptic peptides for each conglutin were monitored, allowing to achieve LODs at low µg/L level. The whole procedure was used to demonstrate the possible migration of allergenic proteins from the lupin-based model material, showing a different tendency of conglutins to migrate in the two simulants investigated. The developed approach is being extended to commercial plant-based FCMs and to other allergenic proteins/ingredients for untargeted identification by LC-high resolution (HRMS) technique of proteins migrated into food simulants; this would allow to gain in-depth knowledge on the allergenic risk associated to bio- and plant-based materials.

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Acknowledgements:

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O6-MS

HEAT-INDUCED LIPID MODIFICATIONS IN *PISTACIA VERA* BY MAILLARD REACTIONS

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Pistachio (*Pistacia vera L.*) consumption, including its use in processed food preparations, has experienced significant global growth due to its pleasant taste and nutritional benefits[1]. Maillard reaction (MR) is a complex set of chemical reactions that occur between reducing sugars and amino acids or proteins when exposed to heat[2]. Initially, a sugar molecule undergoes a condensation reaction with an amino group, resulting in the formation of a glycosylamine, an intermediate that undergoes further rearrangement including dehydration, fragmentation, and a wide range of by-products[3]. While extensively studied using proteins[4,5], the impact of MR on lipids such as phosphatidylethanolamine (PE) is still lacking[6].

In our study, we made an interesting discovery regarding unknown MR products in roasted pistachios. By analyzing the high-resolution MS and MS/MS spectra obtained by LC-MS in both negative and positive ion modes, we identified these reaction products as generated by the condensation of furan-2-carbaldehyde, also know as furfural (C_5H_4O), and phosphatidylethanolamine (PE) species. In vitro simulations of the MR between PE 18:1/18:1 (M) and furfural were performed by heat-induced reactions, and the generation of the following compound ($M+C_5H_2O_2-H_2O$) was ascertained. Along with their *m/z* values, the retention times of the reaction products were found to align with those observed in roasted pistachios when injected into a HILIC column. Additionally, the MS/MS spectra obtained in both positive and negative ion modes exhibited a remarkable similarity. These findings definitively confirmed the chemical structure of one of the observed reaction products. Further work is currently underway to determine the molecular structures of the other isomeric by-products. This study serves as a foundation for a comprehensive investigation of heat-induced lipid modifications; their implications for human health are yet to be fully understood.

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O7-MS

MASS SPECTROMETRY ANALYSIS OF QUORUM SENSING MOLECULES IN SAMPLES FROM PATIENTS WITH SEPTIC SHOCK

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The study here presented showed the LC-MS quantification of molecules of bacterial origin in biological samples from patients suffering of septic shock. These molecules, known as Quorum Sensing (QS), are possible biomarkers of critically ill patients admitted to intensive and sub-intensive care units. Liquid Chromatography-Mass spectrometry (LC-MS) is a powerful technique of high diagnostic significance that has recently been introduced in multiple diagnostic determinations in the clinical setting[1]. Innovative research conducted by MS allowed to identify and study the QS molecules involved in the development of the acute kidney injury (AKI)[2]. Gram negative bacteria were recognized as the major responsible of infections related to AKI. It is known that they secerned a high amount of QS molecules: N-(3-oxododecanoyl)-L-homoserine lactone (C12-AHL), N-butanoyl-L-homoserine lactone (C4-AHL) and 2-heptyl-3-hydroxy-4(1H)-quinolone (C7-HQ). An early developed UPLC-MRM method[3] was here applied to biological samples (plasma and urine) from sub-intensive patients for the quantitation of C12-AHL, C4-AHL and C7-HQ at different time points after the hospitalization in (sub)intensive care units. The aim was to identify and quantify the selected biomarkers and the possible source of the infection leading to the use of a targeted antibiotic therapy. The analytes were extracted from biological samples using a liquid-liquid extraction with ethyl acetate. The extraction yield was evaluated both in plasma and urine samples. For the quantitation of the molecules, we used calibration curves obtained with standard addition method both using urine and plasma matrices. The method was then applied to biological samples at time points of 24-48-96 hours after hospitalization in (sub)intensive care units of patients with septic shock. The results showed the presence (ng/L) of C12-AHL, C4-AHL and C7-HQ suggesting the importance to understand the quantity of bacteria involved in the infection and to modify the antibiotic therapy.

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Oral Elettroanalitica

O1-EL

ANALYTICAL CHARACTERISATION OF DEPOSITS PRODUCED BY PULSED CURRENT

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Pulsed current (PC) and reverse pulsed current (PRC) electroplating is a technique where steady-state (DC) current, the state of the art of any plating process, is replaced with its modulated (non-stationary) forms.

The use of pulsed current is well known as a research tool for studying the electrodeposition mechanism of metals. With increasing emphasis on the properties of the deposits, however, it was realized that this method of deposition could well provide a means of improving their properties[1].

Gold being a noble metal, has a very high resistance to chemical attack. Apart from its chemical stability, owing to desirable electrical properties, gold has been accepted as a versatile material in electronic technology[2]. Electrodeposition of gold or its alloys is not only used in the electronics industry due to its conductive and anti-corrosive properties, but also as a final layer due to its aesthetic properties[3]. For this reason, in recent years, gold has become a promising material in a variety of areas, from jewelry to fashion, art, and furniture. Electrodeposited thin films of gold are generally porous in nature, which may lead to the formation of corrosion products through the pores.

Pulse electroplating has been reported to be effective in fabricating Au materials with higher uniformity, and lower porosity[4]. Also, it is possible to control the composition and the film thickness by regulating the pulse amplitude and width. Most importantly, an increase in the nuclei density could be achieved to obtain electroplated films with finer grains[5].

The aim of this work is to assess how pulsed current changes the chemical-physical characteristics of electrodeposited metal layers of gold, compared to samples produced using DC. In order to highlight any differences between the samples produced by different types of current, various analyses were carried out on them. An aesthetic assessment was made (through colorimetric analysis), but also one concerning morphology and surface properties (XRF analysis for deposit homogeneity, SEM measurements to estimate grain size and AFM evaluation for roughness).

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The authors acknowledge for the support offered by Fondazione CR Firenze, Fondazione per la Ricerca e l'Innovazione dell'Università degli Studi di Firenze and Confindustria Firenze within the FABER4 project.

ELECTRODEPOSITION AND CHARACTERIZATION OF MANGANESE ARSENIDES (Mn_XAs) AS PROMISING CANDIDATES IN SPINTRONICS

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Spintronics is a new branch of electronics in which the spin of the electrons as well as their charge is manipulated to produce a desired outcome. Spintronic devices are particularly attractive for memory storage, magnetic sensor applications, and potentially for quantum computing. Nowadays many efforts are made to increase the efficiency and lower the production costs of these materials, among others the use of molecular inorganic compounds and cheap preparation techniques[1].

Most of these layers are synthesized with physical and/or vapor phase techniques[2] which allow to obtain materials with a very few defects, but which are complex to manage and typically very expensive. For this reason, in this study we have searched for a way to electrochemically deposit a compound with interesting spintronic properties in the aqueous medium. In fact, electrodeposition is notoriously a very cheap, versatile and easily scalable technique. With this purpose Mn-As system was selected thanks to its good magnetic and transport properties to be used as building block for spin valve[3]. MnAs has potential applications in spintronics, for electrical spin injection into Si based devices[4] and DFT simulations predict that Mn_2As and Mn_3As have a low magnetization saturation and a high spin polarization at the Fermi-level[5]. Various precursors solutions, concentrations, supporting electrolytes and pH were tested. The electrochemical behaviour of the precursors was investigated with cyclic voltammetries and both potentiostatic and galvanostatic deposition were carried out. The deposits obtained were morphologically and compositional characterised with scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) and X-ray fluorescence spectroscopy (XRF). The chemical states were analysed with X-ray photoelectron spectroscopy (XPS) and the crystalline structure was investigated with X-ray diffraction measurements (XRD). The preliminary magnetic and transport measurements evidence the promising properties of this deposition process to provide spinfiltering materials.

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O3-EL

Printing Enzymes and Nanomaterials: Water-based Ink Formulation for Stencil-Printing Electrodes

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Developing disposable and low-cost electrochemical devices for biomedical applications has significantly increased with the diffusion of remote diagnostics. This is probably due to the need for regeneration of the conventional sensor surfaces and the demand for production processes that allow the manufacture of disposable and portable electrochemical devices promoting the reduction of the volume of samples, *in-situ* detections, and lower cost. [1]

Conductive inks are used for the development of disposable electrochemical sensors. They trigger the possibility of building screen- or stencil-printed electrodes with similar efficiency with respect to solid electrodes. [2] In particular, biocompatible inks are formulated and stencil-printed on a flexible support that could be easily integrated within smart-devices for the continuous and minimally invasive monitoring of lactate and glucose, as shown in figure 1. First, the conductive ink formulation has been optimized based on electrochemical and rheological measurements implemented within a multivariate analysis model. Afterwards, the active carbon electrode was modified with osmium redox polymers (ORPs) to establish an electronic connection with enzymes, since neither glucose oxidase (GOx) nor lactate oxidase (LOx) are able to directly transfer electrons. [3,4] Finally, both biosensors have been tested in model solution and sweat to determine the analytical figures of merit (*e.g.,* LOD, LOQ, linear range, sensitivity, selectivity, reproducibility, stability, storability *etc.*).

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Research for Innovation REFIN 6CDD3786; PMGB ARS01_01195; ERC Stg2021, GA:101040383; PRIN project prot.2017RHX2E4 ACTUaL"; IDF SHARID (ARS01_01270); University of Galway College of Science and Engineering Scholarship and CSGI are acknowledged for partial financial support.

O4-EL

TOWARDS UNDERSTANDING THE ELECTROCHEMICAL BEHAVIOUR OF 3D GRAPHENE STRUCTURES: FROM SYNTHESIS TO ELECTROANALYTICAL APPLICATIONS

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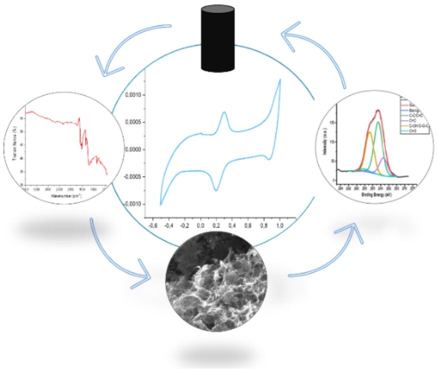
In the last decade, the scientific literature's attention to three-dimensional porous graphene architectures, such as hydrogels and aerogels, has been growing because of their unique structural, chemical, and physical properties. Combined with the well explored brilliant properties of graphene-based materials, 3D graphene structures find application in bioelectronics, sensing, and energy storage [1]. The meso- and macro-porous structure of hydrogels and aerogels allows to overcome some limitation of two-dimensional graphene materials, such as the monolayers re-stacking, conferring unique properties due to the high active surface area of the well-defined three-dimensional graphene architectures [2]. Firstly, in this work we would like to shed light on the chemical behaviour of graphene hydrogels; in particular, according to the flow-chemistry concepts, we propose a facile covalent functionalization strategy through the Diazonium Salts Chemistry. Samples have been extensively characterized via Micro-Raman and ATR-FTIR Spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and BET. Secondly, we studied the electrochemical performances of the 3D porous graphene hydrogel and aerogel structures through Cyclic Voltammetry (CV), Differential Pulse Voltammetry (DPV) and Electrochemical Impedance Spectroscopy (EIS), focusing on the electrochemical sensing properties of the 3D self-standing structures.



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PRINT-LIGHT-SYNTHESIS OF GOLD THIN FILM ELECTRODES FOR ELECTROCHEMICAL SENSING

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The fabrication of Au thin film electrodes by inkjet-printing or screen-printing is traditionally a two-step process, in which i) a gold nanoparticle (NP) ink is deposited on a substrate and then ii) thermally treated to obtain a conductive metallic film. The synthesis and dispersion of NPs cause often practical constraints as agglomerated and aggregated NPs which clog the nozzles of the printhead. Herein, we present the one-step fabrication of Au thin films at room temperature combining drop-on-demand inkjet-printing of a Au precursor ink and simultaneous photochemical reduction of the Au precursor by UV light[1]. The as-obtained Au nanoparticles are well-adhered and do not require any further treatment, because all other ink components escape in the gas phase during printing. This economic process is known as Print-Light-Synthesis (PLS).[2] Thanks to the high flexibility of the process parameters, thin compact Au films as well as films of separated Au NPs can be obtained (Figure 1). We will demonstrate the use of the PLS-Au films as electrochemical sensors for various analytical applications, such as the detection of alcohols and bacterial infection markers. In fact, the PLS-Au electrodes show often a higher sensitivity in respect to commercial screen-printed Au electrodes, opening not only new possibilities for large-scale disposable electrode production, but also for improving sensing.

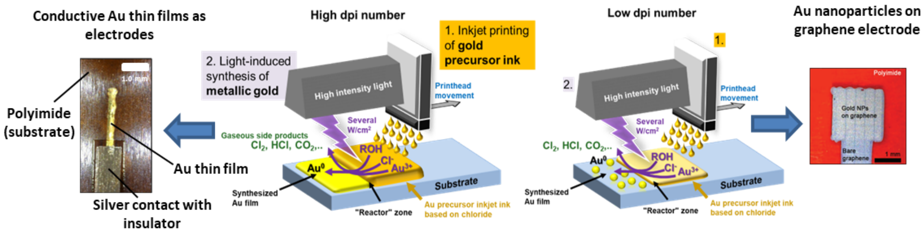

Figure 1: Schematic representation of Print-Light-Synthesis to fabricate compact Au film electrodes (left panels) and Au-NP coated graphene electrodes (right panels).

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Acknowledgements: A.L. acknowledges the support from the Italian Ministry of University and Research (Ministero dell'Università e della Ricerca – MUR).

Oral Equilibri

O1-Eq

LANTHANIDES RECOVERY, FROM AQUEOUS SOLUTIONS, BY BIOSORPTION ONTO *GALDIERIA SULPHURARIA*

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Biosorption is a cost-effective method for removing metal ions from aqueous solutions and if biosorbent material have structural stability at higher acidity, the latter can be also recycled. *G. sulphuraria*, a red alga thriving in geothermal sites with peculiar ecological conditions (i.e., low pH (0.5–3.0), T ≈ 50 °C–55 °C), is one of the best candidates for the biological recovery of metals[1]. The recovering of trivalent Lanthanides (Ce^{3+}, Pr^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Yb^{3+}) from aqueous solutions, by biosorption process onto *G. sulphuraria* lifeless cells, was investigated by potentiometry, UV–Vis, FTIR-ATR spectroscopy and SEM-EDS analysis. All the experiments were performed at 25 °C, in 0.5 M NaCl. A greater biosorption in the pH range $5<pH<6$ can be gained (ranging from 80 μmol/g to 130 μmol/g); the adsorbed Ln^{3+} ions can be recovered at $pH<1$ and, thus, the biosorbent can be reused. The lanthanides biosorption onto *Galdieria* involves specific interactions between Ln^{3+} and functional groups onto surface: praseodymium, samarium, europium, dysprosium, terbium and thulium form bonds with proteins groups; cerium, erbium and holmium interact with carbohydrates groups. This specificity in the mechanism of Ln^{3+} biosorption onto *G. sulphuraria*[2,3] is surprising considering the systematic and stepwise variation of the chemical and physical properties of Lanthanides along the series, making difficult their separation. Furthermore, this study could be of great applicative utility for the trivalent actinides biosorption from waste aqueous solutions. Trivalent lanthanides are used to simulate the trivalent actinides.

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O2-Eq

IRON(III) COMPLEXES OF FLAVANONES IN CITRUS FRUITS: STABILITY, STRUCTURES AND ANTIOXIDANT PROPERTIES

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Citrus fruits are among the most extensively cultivated fruit tree crops in the world. The derived juices are particularly rich in flavonoids, a class of phenolic compounds, which are known to possess several physiological functions related to their antioxidant, antiviral, antithrombotic and anticarcinogenic activities[1]. Besides being able to act as primary antioxidants, donating an H atom to stabilize a radical species, flavonoids can act as secondary antioxidants due to their ability to chelate pro-oxidant metal ions, such as iron (III). This second antioxidant mechanism is related to the interactions between ligand and metal ion and the consequent formation of complexes. Among the various classes of flavonoids, flavanones are characterized by the basic structure shown in Figure 1.

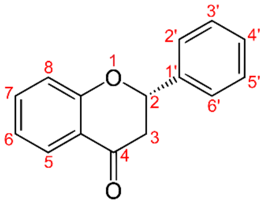

Figure 1: Basic structure of flavanones.

Following our recent studies on the sequestering ability of quercetin and luteolin towards first-row transition metal cations[2-4], herein we present an experimental investigation on the complexation ability of flavanones selected among the major abundant in plant species, namely naringenin and hesperetin, and their respective glycosides, naringin and neohesperidin, towards Fe(III). The stability constants of the complexes were evaluated potentiometrically at 37 °C and in 0.16 M NaCl and the corresponding structures were determined by MALDI-MS approach. To evaluate the competition of the ligands for Fe^{3+} and H^+, the protonation constants of ligands were also determined under the same experimental conditions. Speciation profiles obtained by potentiometric titrations show that in aqueous solution a complexation occurs at 1:1 and at 2:1 ligands-to-Fe(III) ratios.

Moreover, as metal-flavonoid complexes display free radical scavenging activity[5], the antioxidant activities of the Fe(III)-ligands complexes as well as of free ligands were also evaluated.

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O3-Eq

MULTI-TECHNIQUE CHARACTERIZATION AND SPECIATION OF OXOVANADIUM(IV)/8-HYDROXYQUINOLINE-2-CARBOXYLIC ACID AQUEOUS SYSTEM

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Vanadium ions are involved in several biological processes in different organisms and inside the human body[1]. 8-Hydroxyquinoline-2-carboxylic acid (8-HQA) shows interesting features as biological activity and pronounced coordinating abilities[2]. Nevertheless, the interaction between the 8-HQA and the oxovanadium(IV) is still unexplored. The study of the speciation of this system in aqueous solution could expand the knowledge about the complexing abilities of the 8-HQA ligand and the chemistry of oxovanadium metal complexes. In the case of the VO^{2+}/8-HQA system, a multi-technique approach was adopted with the aim of fully characterizing the interactions and the thermodynamic equilibria taking place in the solution. Potentiometric and UV/Vis spectrophotometric titrations were performed, in $KCl_{(aq)}$ 0.2 $mol \cdot L^{-1}$ and T = 298.15 K. Voltammetric experiments and EPR spectroscopy were exploited, to expand the characterization of the system. Since the system showed instability due to the possible oxidation of the VO^{2+} ion at alkaline pH, free-O_2 experiments were conducted to explore the system in the unstable region. Combining the information obtained from all the different techniques, it was possible to achieve a firm understanding of the VO^{2+}/8-HQA system. The main species formed in the solution at various pH were identified. The stoichiometries and coordination mode were hypothesized. Lastly, the stability constants of the complexes were estimated, and the pH stability range established. The results suggest the formation of mainly two metal complexes, [VO(8-HQA)] and $[VO(8\text{-HQA})_2]^{2-}$, in the considered pH range (2 – 6). The complexes are only stable up to pH 6 in aerobic conditions. As reported, to extend the stability of the system O_2 must be excluded.

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Acknowledgements:

This contribution 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)

A MULTIANALYTICAL APPROACH TO ASSESS THE CHEMICAL SPECIATION OF CADMIUM(II) IN THE NORTH SEA

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Marine strategy framework directive has been introduced recently by EU, stating 11 qualitative descriptors to help EU countries to reach a good environmental status (GES), and to defend the marine environment. In 2019, JPI Ocean started a project named "Science for Good Environmental Status" (S4GES) in which an innovative approach for the evaluation of the "Good Environmental Status" was proposed, by monitoring and integrating several physical, chemical and biological information. In this framework, ten samples of sea water were collected during an oceanographic cruise, held in July 2022, in the North Sea outside Belgian coasts. Samples were collected considering tidal currents and distance from the coast to account for the variability of the ecosystem.

In this contribution, the preliminary results obtained to assess the chemical speciation of dissolved cadmium (II) in such samples are discussed. The chemical speciation of a metal cation in a sea water medium can be roughly summarized as follows:

$$c_{Cd} = \left\{[Cd^{2+}] + [Cd]_{inorg}\right\}_{lab} + [Cd]_{org} \tag{1}$$

The total amount of a dissolved metal cation (c_{cd}) was obtained by means of ICP-MS measurements performed on a sample aliquot that was filtered (0.2 μm) and acidified immediately after collection. To obtain other contributions, two kinds of electrochemical measurement were performed on filtered (0.2 μm) undisturbed sample. The first, called "metal titration"[1-5], is aimed at splitting the total dissolved cadmium concentration into that bound to weak labile ligands ($\left\{[Cd^{2+}] + [Cd]_{inorg}\right\}_{lab}$) and to strong organic non-labile ligands ($[\mathrm{Cd}]_{\mathrm{org}}$), together with the conditional constants (log K_{app} or log K') of a generic $\mathrm{Cd(L_{org})}$ species; the second, by means of the 2P-AGNES approach[6-9], is aimed at the determination of the free cadmium concentration ($[\mathrm{Cd}^{2+}]$).

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The contribution was designed and written in the framework of the JPI-Oceans action "Science for Good Environmental Status". We would like to thank the crew of the RV Belgica.

O5-Eq

METHOTREXATE-BASED METAL-COORDINATED ASSEMBLIES RESPONDING TO pH STIMULI: A MULTIPLE EQUILIBRIA STUDY IN SOLUTION AND AT THE INTERFACE

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Methotrexate (MTX) is a methylated derivative of folic acid that is widely employed as a drug in a broad spectrum of diseases, mostly for the treatment of several human malignancies[1]. However, it suffers from poor solubility, short half-life in the bloodstream and drug resistance by targeted cells which strongly affect the drug efficacy. Drug delivery systems have been developed as strategy to overcome the above issues[2]. Among these, polymer-based systems have increasingly gained attention due to their peculiar properties and relatively easy functionalization to respond to specific stimuli[3]. Within this framework, we propose the development of pH-responsive metal-coordinated assemblies containing MTX, biologically relevant metal ions (Cu^{2+} or Zn^{2+}) and polyacrylic acid (PAA), a polymer including functionalities able to respond to pH change. Taking advantage of the pH differences between cancerous and healthy cells, these systems could surmount most of the drawbacks affecting the chemotherapy drug and enhance its bioavailability and efficacy in the controlled/targeted delivery.

The binding features and the energetics of the multiple interactions occurring among the components of the complexes are of key significance for the design and development of the assemblies. All the formation equilibria were investigated in aqueous solution at 25°C and physiological pH by isothermal titration calorimetry which provided a quantitative analysis of the species, binding affinity and their thermodynamic signature. The binding ability of MTX toward the polymer-metal complexes was also examined at the solid-liquid interface by quartz-crystal microbalance with dissipation monitoring. The results gave evidence for the adsorption of MTX onto the polymer-metal layer confirming the complexes ability to interact and release the drug under different pH values[4]. In view of a potential biological application, a detailed investigation of the ability of the MTX assemblies to interact with human serum albumin was also carried out. Overall, the accurate analysis of multiple solution equilibria allowed us the rational design of MTX-based assemblies able to simultaneously enhance the loading and the controlled release of the drug.

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O6-Eq

BE POSITIVE! MORE THAN A STATE OF MIND BEHIND THE THERMODYNAMIC STUDY OF METAL COMPLEXES WITH NOVEL CALCITERMIN PEPTIDE DERIVATIVES

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The antimicrobial peptide calcitermin (VAIALKAAHYHTHKE) has been previously studied by our research group to evaluate its metal chelating ability and bioactivity against various pathogenic microorganisms[1]. To improve the antimicrobial efficacy, some modifications have been introduced in its sequence with the purpose of *(i)* improving membrane permeabilization – by increasing the number of positive charges –, *(ii)* improving the affinity for metal ions, and *(iii)* increasing the proteolytic stability; however, preserving the lipophilic N-terminal portion of the peptide and its original amphiphilic characteristics.

Therefore, we studied the formation of Zn(II) and Cu(II) complexes with the calcitermin derivatives A7R and A8R, where the alanine residues in position 7 and 8 are replaced with arginines, which are known to enhance the antibacterial activity.[2] The A7H analogue has been also considered, to obtain a chelating sequence with four histidines in alternate position. Indeed, the metal-binding affinity not only increases with the number of histidines but, particularly for zinc ion, it is also higher for histidines separated by a single amino acid rather than separated by several amino acids or consecutive[3]. In addition, the A7R, A8R and AH7 peptides, protected by acetylation and amidation at the N- and C-terminus, respectively, have been studied to verify the impact of the terminal protection on the peptide properties, including metal coordination and proteolytic stability. After peptide synthesis and purification, a deep investigation of complex formation equilibria and coordination chemistry of the formed species has been obtained by means of potentiometric titrations, mass spectrometry, UV-Vis and circular dichroism. Enzymatic stability assays provided the half-lives in human plasma of the investigated peptides.

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O7-Eq

INTERACTION OF THE FUNGAL METABOLITE HARZIANIC ACID WITH RARE−EARTH CATIONS

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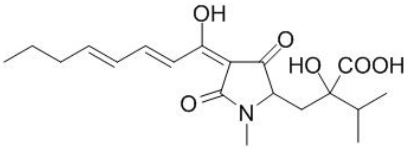

Figure 1

Harzanic acid is a secondary metabolite belonging to the subgroup of dienoyl tetramic acids, essentially produced by fungi of Trichoderma genera (Figure 1). This metabolite is particular regarded for its valuable biological activities (e.g. antimicrobial, plant growth−promoting[1]) which are also related to its chelating properties. In this work, the complexing properties of harzianic acid (H_2L) toward some rare−earth elements (La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Ho^{3+} and Tm^{3+}) have been studied because these elements are emerging contaminants of soil and water bodies which destiny in the environment and effects on organisms is modulated by their interactions with natural ligands produced by bacteria, fungi and plants. Preliminary to chelating properties has been studying the acid−base behaviour of ligand conducted by UV−Vis spectrophotometry titrations. The measures have been investigated at 25 °C in CH_3OH/0.1 M $NaClO_4$ (50/50 *w/w*) as ionic medium, in according to the low solubility of this metabolite in water ($< 10^{-6}$ M), The data collected and processed by numerical methods[2] agree with the following protolysis constants:

$$H_2L + H_2O \leftrightarrows HL^- + H_3O^+ \qquad \log K_{A1} = -4.08 \pm 0.02$$

$$HL^- + H_2O \leftrightarrows L^{2-} + H_3O^+ \qquad \log K_{A2} = -5.63 \pm 0.04$$

The study of coordination properties has been investigated using mass spectrometry, circular dichroism, UV–Vis spectrophotometry, and pH measurements. In particular, the experimental data obtained by UV−Vis titrations and elaborated by numerical procedure[2], can be satisfactorily explained by assuming, for all investigated cations, the formation of a mono−complex (LnL^+) as well as with a bis−complex (LnL_2^-). Since Gadolinium is the element that raises the most concern among lanthanide elements, its effects on organisms at different levels of biological organization were explored, in the presence and absence of harzianic acid. Results of ecotoxicological tests suggest that harzianic acid can decrease gadolinium biotoxicity, presumably because of complex formation with Gd^{3+}.

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O8-Eq

GALLIC ACID FOR THE SEQUESTRATION OF ORGANOMETALS IN AQUEOUS SOLUTIONS

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Gallic acid is a naturally occurring polyphenol present in citrus fruit peels, in grapes, hops, oak bark, green tea, displaying antioxidant properties[1].

This contribution reports preliminary results from an investigation on the acid-base properties of gallic acid and its interactions with two seawater pollutants, namely CH_3Hg^+ and $(CH_3)_2Sn^{2+}$, also with the purpose of exploring its potential as a sequestering agent for organometals in environmental matrices.

Potentiometric, UV-Vis spectrophotometric and spectrofluorimetric titrations were carried out at different temperatures ($288.15 \leq T/K \leq 318.15$) and ionic strengths ($0.10 \leq I/\text{mol dm}^{-3} \leq 1.00$) in NaCl ionic medium, the principal inorganic constituent of many natural fluids[2]. The analysis of the acid-base data allowed the determination of the ligand protonation constants, which were found to be in good agreement with literature findings[3]. The enthalpy change values were also determined.

For each organometal/gallic acid system, speciation schemes featured by protonated species, 1:1 stoichiometry complexes and hydrolytic mixed species were determined. Gallic acid showed a higher complexing ability towards $(CH_3)_2Sn^{2+}$ with respect to CH_3Hg^+. The dependence of the thermodynamic parameters on ionic strength and temperature was modelled using an extended Debye-Hückel type and the Van't Hoff equations, respectively.

Furthermore, the ligand sequestering ability and the affinity towards the selected cationic contaminants were investigated by means of the calculation of $pL_{0.5}$[4] and pM[5] parameters at various conditions including pH ~ 8.1 and $I \sim 0.70$ mol dm^{-3}, which are characteristic of seawater.

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O9-Eq

HYDROXYPYRONES FOR OXOVANADIUM(IV) COMPLEXATION

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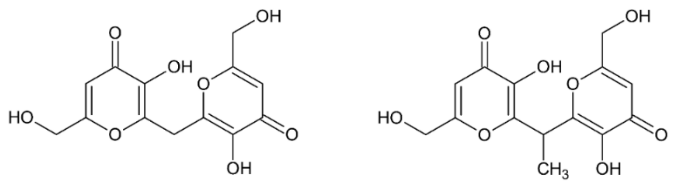
Vanadium compounds have long been recognized for their pharmacological human activities. Among them, hydroxypyrones (HOPs) are very promising ligands, mostly those formed by 3-hydroxy-2-methyl-4H-pyran-4-one (maltol) and 3-hydroxy-1,2-dimethylpyridin-4(1H)-one (deferiprone, DFP)[1]. In this regard, solution equilibria studies of oxovanadium(IV) complexes of two tetradentate HOPs (L1 and L8) are presented. The joint use of potentiometry, UV spectrophotometry, EPR spectroscopy and DFT calculations gives evidence of the formation of 1:1 complex first, and then the binuclear one at very acidic pH. Moreover, two symmetrical intramolecular hydrogen bonds between the hydroxymethyl groups and the coordinating water have been identified. Finally, the interaction with proteins, such as lysozyme have been investigated by docking studies.



L1

L8

Figure 1: Chemical structures of ligands with acronyms: L1 (6-5-hydroxy-2-hydroxymethyl-pyran-4-one]-5-hydroxy-2- hydroxymethyl-pyran-4-one; L8 (2-2′-Ethanediylbis(3-hydroxy-6-(hydroxymethyl)-4H-pyran-4-one)).

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O10-Eq

MEDIUM AND IONIC STRENGTH DEPENDENCE OF FORMATION CONSTANTS. THE “PURE WATER” MODEL

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Several models exist to take into account the dependence of activity coefficients (and, in turn, of stability constants) on system conditions, with particular reference to ionic strength and temperature (since most reactions occur at ambient pressure, dependence on the latter assumes relevance in just particular cases like, e.g., in geochemical studies). However, the most common theories and approaches (e.g., Davies, Bromley, Pitzer, Specific ion Interaction Theory – SIT) can be considered as evolutions of the (Extended) Debye-Hückel equation. All of them have pros and cons, so that none can be considered better than others[1]. Between the ’80s and ’90s, the group of Prof. Silvio Sammartano from the University of Messina proposed, with the precious support of colleagues from the Italian Universities of Torino, Catania and Palermo, a model[2] (with the relative equation), for the ionic strength (and temperature) dependence of formation constants, based on three simple assumptions: [H1]: It is possible to express the dependence on ionic strength of formation constants by a simple equation, independently of the type of reactants and products, and dependent on the type of reaction only.[H2]: All the deviations from the predicted behaviour are ascribed to weak complex formation between components and/or species under study and the background ions (e.g., the ionic medium). This implies that “pure water” is considered as reference state, and some ions as non-interacting with the reactants and/or products involved in the studied equilibrium. [H3]: Perchlorate does not interact with cationic species, tetraethylammonium cations (and higher tetraalkylammonium analogues) do not with O-donor ligands, and Na^+ and K^+ do not with N-donor ligands. Evidences collected during more than half a century in those universities demonstrated the validity of this “pure water model”, and showed the potential of this approach to model the speciation of several multicomponent complex systems in a very simple way. This contribution describes the main features of the pure water model through some examples, highlighting the theoretical and practical aspects of this approach in the speciation modelling of systems of different complexity, including real systems.

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Acknowledgements:

This contribution 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) and is dedicated to the memory of Prof. Silvio Sammartano, for the unquestionable impact he had in developing research in this and related fields.

SPECIATION STUDY OF Cu(II) WITH LACTIC ACID AND PYRUVIC ACID IN SEAWATER-LIKE CONDITIONS

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In the field of new and sustainable materials for environmental remediation, and specifically of metal sequestration, polymer including membranes (PIM) has caught a certain amount of interest thanks to its versatility and simple preparation. The present contribution reports new developments regarding the study of an ecofriendly, novel membrane made of poly-L-lactic acid (PLLA) and Methyltrioctylammonium chloride (or Aliquat336, an ionic liquid) that serves both as plasticizer and extractant. The membrane was tested as an extraction device of Cu(II) in UV-irradiated sea water and trace level conditions by means of Ligand Exchange-Adsorptive Cathodic Stripping Voltammetry. Extensive studies showed the formation of an ML-type complex in solution with a conditional constants of 10.3 ± 0.1. After a process of elimination to rule out possible complexes with released aliquat and/or carbonates, Lactic Acid and its oxidation product Pyruvic Acid were investigated as possible ligand. Cu^{2+}/Lac and Cu^{2+}/Pyr systems were separately studied by Differential Pulse Anodic Stripping Voltammetry (DP-ASV). In this fashion the formation of copper complexes was studied by observing the shift in the potential of uncomplexed metal peak at $I= 0.7$ mol/dm^{-3}. The shift was induced, at first, by adding known amount of ligand and then performing an acid-basic titration by adding NaOH to account for the formation of both ML_y and $ML_y(OH)_i$ complexes. These experiment, proved the formation of ML complexes for both systems with formation constants of 1.8 ± 0.5 and 3.64 ± 0.02, respectively. An electrochemical reaction that involves the pyruvic acid was also observed and is currently under investigation.

Oral Alimenti

MULTIFUNCTIONAL PROPERTIES OF SHORT- AND MEDIUM-CHAIN PEPTIDE MIXTURES FROM HEMP SEED AGAINST METABOLIC SYNDROME

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Over one-third of U.S. adults have a combination of health problems collectively known as metabolic syndrome (MetS). MetS refers to a cluster of conditions that occur together, leading to three main long-term medical conditions, i.e., type II diabetes, ischemic stroke, and cardiovascular diseases, representing the first cause of death globally[1]. Management of MetS involves a dual approach that combines lifestyle changes and a long-term medication regimen, often involving administering several expensive drugs[2]. In this context, the discovery of bioactive compounds for developing new functional foods beneficial for the prevention of MetS has great potential. In this work[3], a dedicated analytical platform was developed to isolate and characterize short peptide sequences produced from hemp seed proteins. The Alcalase® hydrolysate was subjected to peptide separation using two different protocols, namely size exclusion chromatography (SEC) and membrane ultrafiltration (UFM). The first one allowed obtaining two fractions containing medium and short-chain peptides while using UFM, with a molecular cut-off <1kDa, a single fraction consisting of only short-chain peptide mixture was obtained. The fraction containing short-chain peptides was analyzed by a suspect screening untargeted approach based on ultra-high-performance liquid chromatography coupled with high-resolution mass spectrometry (UHPLC-HRMS). At the same time, a typical proteomics experiment by nanoLC-HRMS was employed to analyze the fraction containing medium-chain peptides. After careful manual validation, 559 short peptides and 557 peptides were tentatively isolated in hemp seed by SEC and UFM, respectively. The biological activity of the hemp seed hydrolysates was tested for the bioactivities directly related to metabolic syndrome. Our results indicated that the short-chain peptide mixture was about three times more active than the medium-chain peptide mixture and total hydrolysate concerning measured inhibition of the angiotensin-converting enzyme. The short-chain peptide mixture was also two times more active as a dipeptidyl peptidase IV and two-fold more active on the cholesterol metabolism pathway through the modulation of the low-density lipoprotein receptor.

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O2-ALI

FORMULATION OF BITTERS AND FOOD SUPPLEMENTS STARTING FROM EXTRACTS OF PLANT BLENDS (CONVENTIONAL PROCESS) AND BLENDING EXTRACTS OF SINGLE PURE PLANTS

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The conventional process to produce bitters and food supplements foresees, as a first working phase, the extraction of vegetables in a hydroalcoholic solution of a well-defined mixture of plants using maceration (or infusion) as a traditional solid-liquid extraction technique. The time required for the extraction process is generally between one and four weeks using conventional techniques. Official Pharmacopeia indicates that plants must be extracted by maceration for twenty-one days to obtain the highest yield of extraction of active principles. The innovative experimental design that led to this contribution aimed to evaluate whether it was possible to obtain the same extract, starting from the extraction of single pure plants, obtained under the same operating conditions, and mixing these extracts in the right percentage proportions of mixed plants. The advantage of having pure plant extracts consists in the fact that the mixing possibilities of the extracts are almost infinite, and the process makes them independent of the single traditional recipe. This work reports the results obtained by comparing the extraction of the blends of plants with the extract obtained by blending the extracts of the single plants using two techniques, such as conventional maceration and rapid solid-liquid dynamic extraction (RSLDE) which is based on the use of Naviglio Extractor[1,2,3]. In particular, the plants chosen for this experimentation were: rosemary, sage, laurel, and the extraction while the solvent (extractant liquid) was 96% (v/v) ethyl alcohol, for a first series of tests, and 40% (v/v) ethyl alcohol, for a second series of tests, generally used to produce commercially available bitters.

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O3-ALI

DETECTION OF PERFLUOROALKYL COMPOUNDS IN FOOD MATRICES: ANALYTICAL ISSUES AND FUTURE CHALLENGES

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Per- and polyfluoroalkyl substances (PFASs) belong to a class of synthetic compounds that have attracted public attention since the late 1990s, starting to be recognized as hazard for environment and human health. The strength of carbon-fluorine bond justifies the resistance to metabolic, chemical or thermal degradation and the stability in the environment, thus PFAS has been named "forever chemicals". PFASs can be detected in many food matrices because of their persistence in the environment. In fact, they can contaminate groundwater, surface water and biota. For this reason, PFASs can be found in food of animal and vegetable origin, because of their bioaccumulation through the food chain. After the EFSA opinion of 2020 on the risk to human health related to the presence of perfluoroalkyl substances in food, European Commission published a Regulation regarding maximum levels of PFOS, PFOA, PFNA and PFHxS in certain animal foodstuffs[1]. Since regulation requests to detect these chemicals at low concentrations (pg g^{-1}), efforts were focused to develop a high sensitive and selective method in complex matrices. A solid phase extraction (SPE) was used to clean-up the samples followed by ultrahigh performance liquid chromatography (UHPLC) system coupled to a high-resolution mass spectrometer (Q-Orbitrap)[2]. Some critical key issues linked with PFAS analysis were encountered as the blank contamination due to the ubiquity of these compounds in the laboratory environment as well as in the equipment used during analytical process. Moreover the quantification of the sum of linear and branched stereoisomers was addressed considering branched compounds summed with the linear isomers. The aim of this work was to optimize the performance of the analytical method to achieve the fitness–for-purpose requirements.

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O4-ALI

DEVELOPMENT OF A μ-SPE METHOD FOLLOWED BY UPLC-MS/MS ANALYSIS FOR THE DETERMINATION OF PHOMOPSIN A IN RAW LUPIN SAMPLES.

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Phomopsins are a family of mycotoxins, among which Phomopsin A (PHO-A) is considered the main toxic secondary metabolite produced by the pathogenic fungus *Diaporthe toxica* (or *Phomopsis leptostromiformis*). This fungus mainly occurs in worldwide economically important crops, especially in lupin plant (*Lupinus* spp.), which is its main host and consequentially the major source of animal exposure to phomopsins[1]. PHO-A is a hexapeptide presenting a 13-membered ring with three amino acids linked in a macrocycle with a tripeptide tail, terminating in a dicarboxylic acid; this toxin can bind with high affinity to tubulin isotypes and can disrupt microtubular functions, causing lupinosis, a disease that primarily affects the liver and kidney in various species, particularly ruminants, also suggesting a potential relevance to human diseases. The presence of PHO-A in lupin and its derived products, which are employed in both feed and food applications, could pose potential risks to humans and animals health, so their exposure should be kept as low as possible. This led to the establishment of a legal maximum level for PHO-A of 5 μg/Kg in lupin seeds and their products by the Australian and New Zealand Food Authority as well as by the Food and Agriculture Organization[2].

There are few methods in the literature about the determination of PHO-A in lupin matrix; they include the use of immunoassays, such as ELISA test and high performance liquid chromatography coupled with ultraviolet detection (HPLC-UV), but methods involving the use of HPLC coupled with mass spectrometry (MS) were not fully explored[3].

In this work, a robust and sensitive method for the quantification and determination of PHO-A by means of ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC-MS/MS), was developed. It involved an appropriate sample pre-treatment consisting of an efficient extraction from lupin sample followed by a selective clean-up step carried out by Micro Solid Phase Extraction (μ-SPE), in order to lower matrix effect with minimal amount of sample and solvents; it was coupled with a suitable enrichment factor, aimed at lowering the limit of quantification (LOQ) value, guaranteeing the quantification of the analyte even below the regulatory limit.

The presented method was validated according to the international guidelines and applied on raw *Lupinus albus* L. samples.

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O5-ALI

A GREEN AND INNOVATIVE APPROACH BASED ON COLLOIDAL ANALYSIS TO ASSIST WINE GROUPING

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Wine is one of the most important foodstuffs all over the world: it is crucial to develop analytical methods able to analyze and group cultivars and products, to detect origin and adulterations. At the same time, the use of environmentally-heavy reagents and solvents should be avoided to adhere to greenness standards, especially when large volumes of samples need analyzing. Developing green, high-throughput and high data-yielding analytical methods for wine analysis is a key objective. Wine is a hydroalcoholic colloid characterized by the presence of proteins, polysaccharides and polyphenols that also interact with each other, creating various supramolecular specimen [1]. In this work, two datasets were compared, to understand the applicability of greener approaches to wine analysis and grouping. The first derived from classical chemical analyses, that are time-consuming and expensive; the second was obtained from Asymmetrical Flow Field Flow Fractionation (AF4) – multidetection, and focused on the colloidal portion of the samples. Both were elaborated with chemometric approaches. The results interestingly highlighted that it is possible to achieve better sample discrimination from a limited number of AF4 analyses compared to the multiple traditional techniques. Overall implementing the study of “green” AF4 information on wine colloidal content may represent a substantial improvement towards discrimination and identification of adulterations.[2]

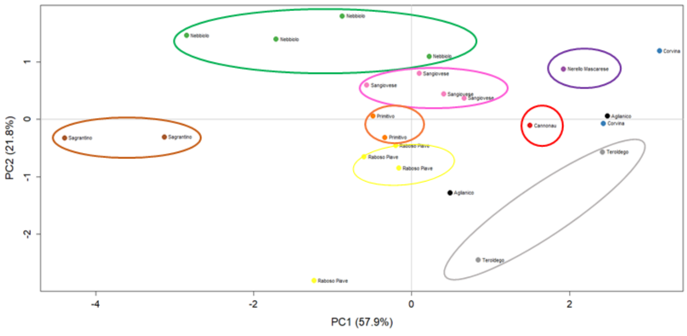

Figure 1: Scores-plot of wine cultivars from AF4 data.

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IDENTIFICATION AND QUANTIFICATION OF COENZYME Q10 AND VITAMIN K1 IN BRASSICA MICROGREENS AND BABY LEAVES BY LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY COUPLED WITH ATMOSPHERIC PRESSURE CHEMICAL IONIZATION

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Microgreens are young and tender vegetables that are typically harvested within 10-20 days of the seedlings' emergence. They grow to a height of approximately 5 cm and display fully expanded cotyledons and the initial pair of true leaves at different stages of development. In comparison, baby leaf vegetables are more mature and larger than microgreens. They are harvested after 20-40 days, once the young leaves, limited to a maximum of eight, have fully developed.[1] Recently, these alternative vegetables have gained recognition due to their rich content of minerals, vitamins, antioxidants, bioactive compounds, and other beneficial components.[2] Evaluating the levels of coenzyme Q10 (CoQ10) and vitamin K1 in both microgreens and baby leaf vegetables can significantly contribute to our understanding of the health benefits associated with their consumption. CoQ10, a vitamin-like substance, plays a vital role in essential cellular processes such as mitochondrial electron transfer and ATP production.[3] Similarly, vitamin K1 is crucial for blood coagulation and is used in the treatment of hemorrhagic disorders. In this study, we investigated two varieties of microgreens and baby leaf vegetables belonging to the *Brassicaceae* family, specifically *Brassica rapa* L. (*subsp. sylvestris* L. Janch., *var. esculenta* Hort) and *Brassica oleracea* (*var. acephala*). These vegetables are commonly found in the Apulia region of southern Italy. Our objective was to analyze and quantify the levels of CoQ10 and vitamin K1 in both microgreens and baby leaf vegetables. To accomplish this, two different extraction protocols with and without saponification were employed. The extracted samples were then analyzed using RPLC coupled with high-resolution/accuracy mass spectrometry with atmospheric pressure chemical ionization (RPLC-APCI-FTMS). Tandem mass spectra confirmed the identity of the analytes and was very helpful to identify other nutraceutical compounds with similar molecular structures. By employing this approach, we aimed to gain insights into the presence and quantity of CoQ10 and vitamin K1 in the examined microgreens and baby leaf vegetables.

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This work was supported by Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 341 of 15 March 2022 of Italian Ministry of University and Research funded by the European Union – Next Generation EU. Project code PE00000003, Concession Decree No. 1550 of 11 October 2022 adopted by the Italian Ministry of University and Research, CUP D93C22000890001, Project title “ON Foods - Research and innovation network on food and nutrition Sustainability, Safety and Security – Working ON Foods”

O7-ALI

NUTRITIONAL VALUE OF HOUSE CRICKET (*ACHETA DOMESTICUS*) FED DIETS SUPPLEMENTED WITH DIFFERENT LEVELS OF THE SEAWEED *PALMARIA PALMATA* IN THE FEEDING MEDIA

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In the last ten years, insects have been identified as promising alternative sources of protein for the feed and food sectors, being highly nutritious and, at the same time, more sustainable than traditional animal farming when it comes to resource use and their overall ecological footprint[1]. The house cricket (*Acheta domesticus***,** AD, Orthoptera: Gryllidae), recently authorized by the European Commission as novel food (EU 2022/188), is one of the most nutritious insect species, being rich in protein, lipid, and both macro- and micronutrients[2]. However, being a terrestrial species, it lacks long-chain polyunsaturated fatty acids, such as the omega-3 eicosapentaenoic (EPA, 20:5n3) and docosahexaenoic (DHA, 22:6n3) acids, which are health-promoting nutrients for human consumption. The chemical composition of insects strongly depends on the feeding media[3], then would be possible to study the introduction of appropriate ingredients into the rearing substrate to increase their nutritional value. This study aimed to investigate the proximate and nutrient composition of AD reared on substrates containing different percentages (5%, 10% and 20%) of an underexploited eco-sustainable species of seaweed such as the red algae *Palmaria palmata*, known to contain high-quality nutrients with health-promoting properties[4]. Fatty acids were determined by gas chromatography-mass spectrometry, while amino acid analysis was performed by HPLC. Results demonstrated that the inclusion of *P. palmata* in the cricket's diet significantly contributed to increase its nutritional value in terms of : i) omega-3 fatty acids, with the detection of EPA (absent in the control group); ii) protein content, with a good presence of essential amino acids and an increase up to 54.2±0.8 g/100 g dry weight (dw) at 20% inclusion of *P. palmata vs* 51±1 g/100 g dw of the control group.

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O8-ALI

NIAS MIGRATION STUDY FROM POLYMERIC MATERIAL TO DRY FOOD

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NIAS are compounds not added for a technical reason during the manufacturing process in materials that can migrate when the artefacts are in contact with food. Monitoring and controlling consumer exposure to these substances is therefore essential to ensure the safety of food products.

Aniline, acetyltributylcitrate, bis(2-ethylhexyl)adipate, 2,6-di-tert-butyl-hydroxytoluene (BHT) and 1,4-butanediol migrations from a polyurethane manufact, used as a gasket in contact with dry food matrices, into Tenax®, the food simulant required by the legislation[1], and into six different food matrices (rice, flour, powdered milk, cocoa powder, sugar, corn starch) were studied.

The aim of this study is the optimization and validation of the analytical method that allows the identification and quantification of the specific migration of such analytes, which could occur following contact of a polymeric product with dry foods.

Contact tests are performed by contacting the polymer to be tested with the simulant food and the other food matrixes in an oven at 70 °C for 3 days to simulate the worst conditions in the real application[2]. The quantitative analysis is carried out using the gas chromatography technique hyphenated to the mass spectrometry. Recovery tests are performed to evaluate the efficiency of the method. The results obtained show that the process is influenced not only by the chemical nature of the migrant, but also by the physical-chemical nature of the simulant or food matrix used.

Fig. 1. Migration test with food simulant preparation

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SINGLE-LABORATORY VALIDATION OF THE ThRAll METHOD FOR MULTIPLE ALLERGEN DETECTION IN CHOCOLATE

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Mass spectrometry has been widely accepted as confirmatory tool for the sensitive detection of undeclared presence of allergenic ingredients. Multiple methods have been developed so far, still lacking of harmonization of the analytical validation and impairing comparability of results. In this frame, the European Project ThRAll funded by EFSA was designed to develop a prototype MS-based reference method for multiple allergen detection in complex food matrixes[1]. Preliminary data about materials characterization and method development were recently published[2-4].

In this contribution, the results of a rigorous single-laboratory validation of the MS-based method for the quantitative detection of six allergenic ingredients (milk, egg, peanut, soybean, hazelnut and almond) in a chocolate based matrix will be presented. The method performance characteristics were assessed according to official considerations issued by the European Committee for Standardization[5]. Synthetic surrogates of the peptide markers (native and isotopically labelled) have been used in matrix matched calibration curves as external calibrants. Conversion factors for all six allergenic ingredients have been determined for the first time to report the final quantitative information as mass fraction of total protein of the allergenic ingredients per matrix, being such reporting unit exploitable in allergenic risk assessment plans. Different samples of chocolate bar incurred at four defined concentration levels close to the currently available threshold doses have been analysed to test the quantitative performance of the analytical method, with a proper estimate of the measurement uncertainty from different sources of variability. The sensitivity achieved resulted in compliance with the various threshold doses issued or recommended worldwide.

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Acknowledgements:

This project has received financial support from the European Food Safety Authority (EFSA), Grant GP/EFSA/AFSCO/2017/03. The present communication, however, is under the sole responsibility of the authors. The positions and opinions presented in this article are those of the authors alone and do not necessarily represent the views/any official position or scientific works of EFSA. To find out more about EFSA guidance documents and other scientific outputs of EFSA, please consult its website at: http://www.efsa.europa.eu.

Poster

Sensori e Biosensori

SB-P1

L-PROLINE DETERMINATION IN RED AND WHITE WINES USING NEW VOLTAMMETRIC SENSOR BASED ON LDH AND H_2O_2

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Our research group has developed a simple, fast, and inexpensive voltametric system for determining proline concentration both in standard solutions and in real samples (red and white wines), taking inspiration from our recent work in which a new sensor for hydrogen peroxide was proposed[1,2]. This new system uses a non-enzymatic sensor based on a working electrode of glassy carbon (GC), modified with a layered double hydroxides (LDHs) compound, which can be schematized as (Zn-Al -NO_3), of the type GC-$Ag_{(paste)}$-LDH-H_2O_2, (with hydrogen peroxide in solution at fixed concentration), and operating by three electrode cyclic voltammetry format. In fact, our research group obtained, in previous work[2] excellent sensors for hydrogen peroxide, using LDH compounds, in solutions containing L-proline at a fixed and optimized concentration, although the role of proline in these sensors has not yet been fully clarified, we believe, that proline acts positively on the electron transfer mechanism. Therefore, we saw the possibility of analyzing, with the same voltammetric sensor, also the unknown concentration of proline present in solution, once the hydrogen peroxide concentration was fixed and kept constant. So, we fabricated a calibration curve, increasing only proline concentration in solution. New method, for L-proline, shown a linearity range, in semilogarithmic coordinates, between 125 mol L^{-1} and 3200 mol L^{-1} of proline, with a limit of detection (LOD) value of 85.0 mol L^{-1} and a limit of quantitation (LOQ) value of 95.0 mol L^{-1}. The developed method is applied to the determination of proline in several samples of commercial Italian wines. The results are compared with those obtained by applying the classic spectrophotometric method of ninhydrin, obtaining a good correlation of the results.

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SB-P2

PAVING THE WAY TOWARD FRESH-CUT FOODS FRESHNESS SENSING BY BIOPLASTIC-BASED OPTODES

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Food packaging industry and food supply chain have been continuously under attack in the last years due to the negative environmental impact of plastic packaging and the large amount of food wasted[1]. These widespread criticisms have pushed researchers and industry to question the order of the things and re-imagine the packaging itself, no longer meant as just disposable and pollutant container but aiming at a reusable or biodegradable solution that can either elongate food shelf-life or provide further information about food degradation[2].

In this scenario, we approached the development of an array of bioplastic-based colorimetric sensors to be applied for shelf-life monitoring of fresh-cut salads or other vegetables, which represent one of the most worrying foods in terms of perishability and safety[3]. We optimised bioplastic composition and casting procedure by Design of Experiments, we identified the most promising receptors for degradation markers detection, among commonly employed pH indicators[4,5], and we directly selected the most promising device in real conditions, i.e. on real fresh-cut foods stored in a domestic fridge. According to the encouraging preliminary results, these smart labels can play a significant role in fresh-cut foods shelf-life monitoring by simple naked-eye detection.

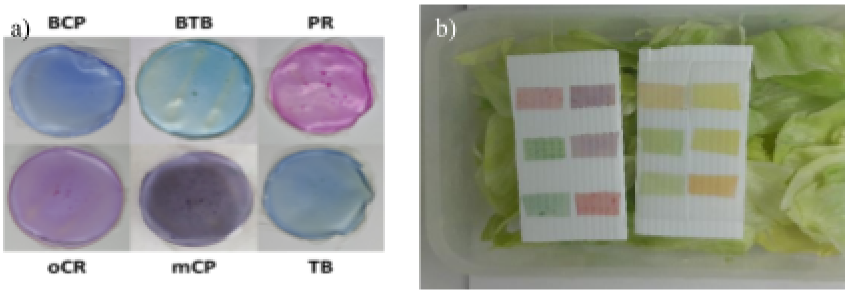

Figure 1: Bioplastic films added with bromocresol purple (BCP), bromothymol blue (BTB), phenol red (PR), *o*-cresol red (oCR), *m*-cresol purple (mCP) and thymol blue (TB) (a); experimental set up for fresh-cut salad freshness monitoring (b)

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DESIGN OF A PAPER-BASED ELECTROCHEMICAL STRIP FOR MIRNA – DETECTION RELATED TO LUNG CANCER

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In the era of liquid biopsy, electrochemical biosensors can offer highly performing, user-friendly and cost-affordable solutions for portable diagnostics of cancer biomarkers. The interest towards microRNAs (miRNAs) as novel diagnostic and prognostic biomarkers is growing, and highly sensitive detection of miRNAs can be achieved with various methods (nucleic acid amplification-based or fluorescence imaging methods)[1]. Among the existing biosensing architectures, electrochemical sensing platforms are showing promising results in the detection of miRNA signatures in complex biological matrices[2]. In this work, a paper-based electrochemical platform for miRNA detection was developed. In the present study, hsa-miR-224-5p was selected as a target for lung cancer early detection, as highlighted in a recent study that has identified miRNA as a promising biomarker circulating in blood[3]. This target sequence was determined by modifying an AuNP-modified paper-based electrode with a single stranded (ssDNA) sequence complementary to the target. The recognition probe was labelled with a redox mediator, namely methylene blue (MB). The sensing platform is defined as "signal off": when the target is absent, the MB attached to the immobilized probe can easily exchange electrons with the working electrode surface, while when the target is present in solution, it produces the formation of a probe-target duplex which limits the flexibility of the system, thus lowering the signal due to the MB exchange of electrons. The presence of hsa-miR-224-5p was monitored following the decrease of the recorded current, and this approach has been also applied to other disease as described previously in literature by our group[4]. All the experimental parameters were optimized, including the ionic strength, the amount of AuNPs, probe density, electrochemical parameters. Finally, the application of square – wave voltammetry (SWV) technique allowed a limit of detection for the selected target in low nanomolar range, with preliminary application in biological matrices.

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BIOSENSING OF CONTAMINANTS IN AGRICULTURE: FROM MULCHES TO SOIL AND CROPS

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One of the most widespread agricultural practices to improve crop and harvest quality is mulching. Mulching films are generally composed of polyethylene (PE), albeit biodegradable films have recently also been used[1]. Plastic mulching may represent a physical and chemical threat for human health and the terrestrial environment since the pollutants transported by plastic mulches (*e.g.*, phthalates, known as endocrine disruptors) could enter the food webs via soil biota and crop plants[2]. Biodegradable plastic mulches have been developed as an alternative: since there is no need to remove them from the field, a reduction of the plastic waste and the costs of collection, treatment, and disposal are envisaged. However, there is still a lack of knowledge on which substances could be released from biodegradable mulches and potentially endanger biodiversity and human health[3]. Taking into account these issues, this work investigates the presence of chemical additives in agricultural soils and cultivated crops resulting from the application of plastic mulching films and biodegradable films and provide information on possible differences among them in terms of chemical transport to plants, potential agricultural soil contamination and changes in soil microbial community. A small-scale experiment has been set up to reproduce the use of mulches under field conditions. A smart biosensing device is developed in order to monitor in a fast and user-friendly way the release of contaminants from the mulches to soil and crop plants. While the biosensor will be sufficiently selective and sensitive to be a point-of-use rapid system, a GC-MS method will be used to validate the results. The temporal dynamics of the soil microbial community will be elucidated using a metagenomics approach.

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Acknowledgements: this research is supported by the European Union-Next GenerationEU, UNIFI Young Independent Researchers Call – MuSC (*Analysis and sensing of contaminants in agriculture: from Mulches to Soil and Crops*).

NANO MOLECULAR IMPRINTED POLYMERS (NANOMIPS) FOR RELIABLE QUANTIFICATION OF D-GLUCONATE IN MUST

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D-gluconate is produced through the oxidation of D-glucose by the metabolism process of various microorganisms. This organic acid is commonly found in vinegar, honey, and wine made from grapes infected by *Botrytis cinerea*. The measurement of D-gluconate in these matrices is essential for ensuring product quality, identifying spoiled products, and improving process efficiency. However, due to the complex nature of these matrices, it is necessary to use selective and precise methods for accurate results. Determination of D-gluconate in foodstuff (see e.g., in must [1]) is traditionally performed by automated enzymatic method and HPLC, but they are time-consuming, requiring tedious sample treatments to be performed. As an alternative, sensors based on molecularly imprinted polymers (MIPs) possess unique features of selectivity, sensitivity, and stability also in complex matrices. MIPs are synthetic materials attracting high interest since they are cheap, easy in preparation, and their production is highly scalable MIPs [2]. The development of MIP nanoparticles (nanoMIPs–imprinted materials < 200 nm diameter) has significantly improved performance of MIPs: the small size of nanoMIPs allows for more regular structures with a high surface area to volume ratio, and a greater yield of useable product which contrasts with the more traditional bulk MIP [2]. Herein, we developed a high-performing nanoMIP-based sensor to detect D-gluconate and tested their efficacy in a sensor platform. The nanoMIPs were synthesised and characterised by Surface Plasmon Resonance (SPR), Dynamic Light Scattering (DLS), Fourier-Transform Infrared Spectroscopy (FT-IR), and Transmission Electron Microscopy (TEM). The performance, reproducibility and selectivity of the D-gluconate sensor was evaluated by Differential Pulse Voltammetry (DPV). The results were compared to the NIP (non-printed polymer) in the concentration range between 0.025 and 5 g/L^{-1} in PBS (50 mM, pH = 7.2). Preliminary results on analytical performances will be reported.

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SB-P6

ELECTROCHEMICAL AND SPECTROSCOPIC CHARACTERIZATION OF SELF-ASSEMBLED MONOLAYERS FOR EGOFET BIOSENSOR DEVELOPMENT

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Self-assembled monolayers (SAMs) were widely studied in the last decades, gaining an increasing interest thanks to their application in different bioelectronic devices as surface plasmon resonance (SPR) and field-effect transistors (FETs)[1,2]. While SAMs are typically employed to effectively immobilize the biorecognition element[3], Macchia et al. proposed also a role in improving device performance by facilitating the formation of a diffuse hydrogen bonding network between the chains[4].

In this regard, a combination of different analytical techniques was exploited, consisting in Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), Differential Pulse Voltammetry (DPV), X-ray photoelectron spectroscopy (XPS) and Grazing Angle – Attenuated Total Reflectance (GA-ATR) Infrared Spectroscopy[5,6]. This approach was used to investigate SAMs conformational reorganization onto an electrode surface due to the application of an electrical field[5], comparing the device electronic characterization with the electrochemical and spectroscopic analyses. Moreover, differential pulse voltammetry (DPV) in NaOH 0.1 M was used to estimate the reductive desorption of functionalized SAMs. 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.

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SB-P7

PORTABLE E-TONGUE BASED ON NANOCOMPOSITE MODIFIED SCREEN-PRINTED ELECTRODES COUPLED WITH CHEMOMETRICS FOR FOOD AUTHENTICITY ASSESSMENT

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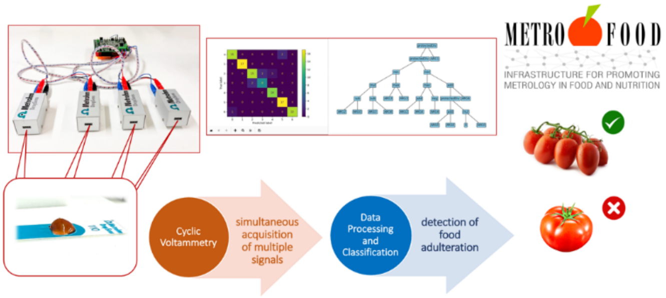
In the context of the research activities undertaken within the "*Strengthening of the Italian Research Infrastructure for Metrology and Open Access Data in support to the Agrifood*" project (METROFOOD-IT) we performed a preliminary study aimed at evaluating the potential of arrays of screen-printed electrodes modified with gold nanoparticles, copper nanoparticles, graphene, carbon nanotubes and conducting polymers for the detection of food adulteration. For this purpose, the discrimination of tomato cultivars of different economic value in both fresh and canned products was taken into consideration. Exploiting the catalytic properties of composite materials consisting of poly(3,4-ethylenedioxythiophene) including metal nanoparticles with respect to the oxidation of antioxidants (ascorbic acid)[1] and sugars (glucose and fructose), promising results in the classification of prized tomatoes, such as "*datterino*" PGI (Protected Geographical Indication) compared to the less valuable and cheaper varieties were achieved. With the aim of developing and validating classification models for food adulteration control, multivariate and artificial intelligence techniques were applied to the potentiostatic and potentiodynamic datasets.



Simultaneous acquisition of the signals was enabled and speeded up by a smart and portable multi-channel potentiostat[2] specially designed within the project.

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We would like to thank METROFOOD-IT project which received funding from the European Union - NextGenerationEU PNRR—Mission 4 "Education and Research" Component 2: from research to business, Investment 3.1: Fund for the realization of an integrated system of research and innovation infrastructures—IR0000033 (D.M. (Ministerial Decree) Prot. no.120 of 21 June 2022).

SB-P8

SMART ELECTROCHEMICAL APTASENSOR FOR ON-SITE DETECTION OF OKADAIC ACID IN SEAFOOD PRODUCTS

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Okadaic acid (OA) is one of the "diarrheic shellfish poisons" produced by the dinoflagellate species *Dinophysis* and *Prorocentrum*. Contamination of shellfish with okadaic acid has been associated with harmful algal blooms throughout the world. OA is able to cause diarrheic shellfish poisoning in humans with symptoms such as diarrhoea, nausea, vomiting, and abdominal pain. Consequently, it is imperative to develop fast, accurate and easy-to-use analytical methods to determine OA in seafood products to safeguard the health of consumers[1].

Electrochemical aptasensors own high specificity and sensitivity thanks to the affinity reaction between the aptamer and the analyte, even in complex matrices; key steps in their development are represented by the immobilization of the aptamer and the signal generation. Therefore, platforms with overall improved electrochemical features that can exploit aptamer probe immobilization in a tailored manner to enable the optimum signal generation are in high demand. In this work, an electrochemical aptasensor for OA detection based on a competitive approach was realized[2]. Disposable graphite screen-printed electrodes were used to obtain a performing device that could be potentially applied for on-site analysis. The conjugation of a polymeric matrix of poly(L-aspartic acid) with nickel nanoparticles was exploited for the ultra-sensitive detection of OA[3,4]. All the steps needed for the realization of the aptasensor were investigated and optimized by electrochemical and optical techniques. The aptasensor was integrated in a smart setup comprising a pocket instrument connected to a smartphone. The platform was used in two configurations for perform drop and microflow measurements for on-site decentralized analysis.

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Acknowledgements: this work is supported by HORIZON-CL6-2021-FARM2FORK-01-10; Grant Agreement n° 1060712.

SB-P9

DEVELOPMENT OF COLORIMETRIC PAPER-BASED ANALYTICAL DEVICES INTEGRATING METAL NANOPARTICLES FOR SMARTPHONE-BASED ANALYSIS

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The implementation of affordable technologies to fabricate optical and colorimetric analytical devices integrating nanomaterials is a compelling challenge for the analytical community. In particular, the controlled decoration of flexible substrates with functional plasmonic metal nanoparticles (MNP), can offer infinite opportunities for the development of (bio)sensors and integrated analytical devices. Herein, an overview on the development of lab-on-paper analytical devices for food analysis exploiting the MNP integration into flexible supports will be presented. Innovative and versatile approaches to fabricating paper-based devices equipped with gold (Au), silver (Ag), platinum (Pt), copper, and nickel nanoparticles as colorimetric sensing elements will be presented. The proposed lab-on-paper devices, designed via low-cost benchtop technologies (i.e., laser/cutter-plotter, thermal-laminator, etc.) using office-grade substrates (i.e., polymeric-sheets, cellulosic substrates, etc.), aim to reduce both analysis and result-readout complexity. Three lab-on-paper devices, where the sensing is based on MNPs integrated into paper substrates and the result readout is obtained with a simple smartphone, will be presented. They will be shown: (i) a three-branched paper device for the extraction-free evaluation of antioxidant capacity and total phenolic content in extra virgin olive oil, where AuNPs and AgNPs are colorimetric probes and the paper-fluidic allow the sampling[1]; (ii) a flip-flop paper-device for the selective determination of ascorbic acid, where PtNPs oxidase-like activity allows a dye-based colorimetric-readout; (iii) a paper multi-MNPs gas sensor array for the monitoring of environmental industrial sanitation, where multi-information are obtained from the different MNPs color changes. This presentation proves how innovative strategies allow the rational manufacturing of within everyone's reaches colorimetric sensing devices suitable for out-of-lab analysis.

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Acknowledgements:
This research was funded by the European Union – Next Generation EU. Project Code: ECS00000041; Project CUP: C43C22000380007; Project Title: Innovation, digitalization and sustainability for the diffused economy in Central Italy – VITALITY

LOW-COST NANOSTRUCTURATION AND MICROFABRICATION APPROACHES FOR ELECTROCHEMICAL DEVICES DEVELOPMENT

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Conventional food analytical methods require skilled personnel and expensive instrumentation; moreover, often cumbersome, time-consuming, and little-green sample pre-treatments are required. Nowadays, the demand for smart and green analytical approaches suitable for on-site/field analysis dramatically increased. In this framework, flexible polymers and cellulosic substrates demonstrated their exploitability, showing outstanding versatility for the fabrication of miniaturized devices for food analysis; however, often the manufacturing technologies result in complex, expensive, and little sustainable. In particular, the production of point-of-need devices integrating nanomaterials (NMs), conceived to achieve high performance, is challenging and not within everyone's reach.

This presentation focuses on the implementation of completely lab-made electroanalytical devices based on functional NMs produced avoiding the use of solvents; the devices are designed to enclose/automate several food analysis steps. Particular attention will be paid to (i) sensing surfaces' nano-structuration via sustainable approaches and (ii) fabrication of disposable devices using low-cost substrates (i.e., polymeric-sheets, paper, etc.) and benchtop microfabrication technologies (i.e., stencil-printing, CO_2 laser scribing/cutting, cutter-plotting, thermal-lamination, etc.). The potential of the developed devices will be demonstrated for food analysis, among others will be presented: (i) a CO_2-laser nanostructured lab-on-strip device for the rapid and extraction-free evaluation of antioxidant capacity (AOC) in extra virgin olive (EVOO), capable of measuring the EVOO AOC in 2 min without pre-treatments; (ii) a CO_2 laser-conceived graphene-based paper 3D pop-up device for direct carbaryl determination in grains, this device enclosed all the analysis steps from sampling to result; (iii) different types of flexible third-generation fructose biosensors based on fully lab-made nanostructured transducers. Eventually, the state of progress of under construction innovative lab-made flexible nano(bio)devices, designed for analysis of food components and contaminants, will be also shown.

Acknowledgements:
This research was funded by the European Union – Next Generation EU. Project Code: ECS00000041; Project CUP: C43C22000380007; Project Title: Innovation, digitalization and sustainability for the diffused economy in Central Italy - VITALITY

SB-P11

ENZYME-BASED CATALYTIC METHODS FOR REAL-TIME ELECTROCHEMICAL ASSESSMENT OF WASTEWATER CONTAMINATION

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Enzymatic catalytic processes offer significant potential for reducing pollutants in wastewater treatment facilities and promoting sustainable bioremediation strategies. Additionally, these processes can be employed to monitor wastewater contamination levels. Urea, a major contaminant in wastewater, is crucial to track due to its widespread use as a fertilizer and cattle feed supplement[1]. Intensive livestock farming contributes to urea entering the environment, primarily through soil runoff, leading to algal blooms and eutrophication[2].

In this study, we propose a real-time urea measurement method that combines enzyme reactors with flow injection analysis (FIA) potentiometric analysis. FIA-based bioreactors are ideal for continuous monitoring and automated sample processing. Various bioreactors were constructed by covalently immobilizing enzymes onto appropriate solid-phase materials (e.g., glass beads, plastic tube inner walls)[3]. These reactors were then connected to solid-state ammonium sensors for electrochemical readings.

Analytical performance was assessed based on factors such as cross-linker concentration, immobilized enzyme quantity, and flow rate. The FIA system was optimized to achieve maximum signal in minimal time. Key analytical parameters, including sensitivity, linear range, repeatability, and lifetime, were evaluated. Matrix effects were also examined, and a clean-up procedure to mitigate potential interferences is expected.

Ultimately, the FIA system should be fully automated, from sampling to result generation, enabling its installation at strategic locations within wastewater treatment plants for real-time monitoring.

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SB-P12

DNA-FUNCTIONALIZED CARBON NANOTUBE ELECTRODES AS NOVEL E-CRISPR PLATFORMS

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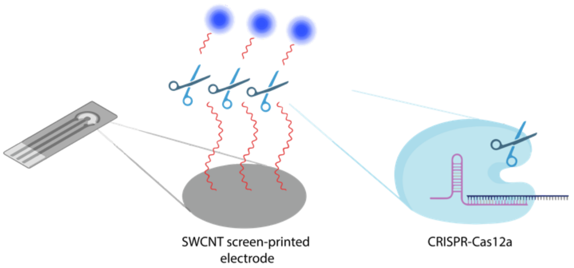
In recent years, CRISPR-Cas systems have emerged as powerful tools in the design of high-performing analytical devices, enabling novel strategies in nucleic acid diagnostics. Integrating CRISPR-Cas12a technologies with electrochemical biosensing (E-CRISPR) has demonstrated the potential for the development of rapid and cost-effective point-of-care biomolecular assays.[1] To transduce the target-responsive non-specific nuclease activity of CRISPR-Cas12a into an electrochemical signal, redox-tagged single-stranded DNA (ssDNA) probes can be covalently attached to the electrode surface, leveraging a signal-off output upon enzymatic cleavage. Here, we describe a new prototype of an E-CRISPR platform based on single-walled carbon nanotube (SWCNT) screen-printed electrodes. These nanostructured carbon-based electrodes are cheaper than standard gold electrodes, possess intrinsic electrocatalytic properties and high conductivity, showing high versatility in the design of E-DNA platforms.[2,3] Yet, their integration with CRISPR-Cas-based strategies remains to date unexplored. In response to this, we have functionalized the surface of these electrodes with a set of rationally designed methylene blue-tagged ssDNA probes varying in length and structure, including both linear and hairpin configurations, studying the impact of these structural changes on the measurable current signal. We then investigated the extent of the trans-cleavage activity of an active Cas12a-crRNA complex by directly incubating the complex on different DNA-functionalized platforms, to identify the configuration maximizing the signal-to-noise ratio. The designability of the dsDNA CRISPR-Cas12a activator enables the development of E-CRISPR biosensors for diverse nucleic acid targets. The DNA activator can also be designed as a transducer for the detection of protein-based inputs. The programmability of these systems, combined with the attractive properties of nanostructured carbon-based materials, can enable significant advancements in electrochemical biosensors.



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SB-P13

QUALITATIVE DETECTION OF HEAVY METAL IONS THROUGH FUNCIONALIZED AgNPs BY EXPLOITING MULTIVARIATE CURVE RESOLUTION-ALTERNATING LEAST SQUARES ANALYSIS

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Heavy metal poisoning of water is a major environmental concern with detrimental consequences for organisms, plants and humans that are exposed to it. [1] The development of colorimetric sensor that allow the rapid, real-time, sensitive, and selective determination heavy metals is therefore crucial to mitigate the risk related to the presence of heavy metal ions. In this work we present a colorimetric sensor based on functionalized silver nanoparticles for the detection of metal ions in solution. The interaction between the target metal ion and the functionalizing agent triggers the aggregation of these nanoparticles, and the consequent change in optical properties allows the detection/quantification of the analyte. [2] In detail, Ag-nanoparticles were synthesized by the chemical reduction method, and successively functionalized with mercaptoundecanoic acid. Their ability to detect metal ions were investigated by monitoring the UV-Vis spectra upon the titration of the Ag-nanoparticles suspension with the metal ions of interest (Ni^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Mn^{2+}, and Cu^{2+}). The raw UV-Vis spectra obtained from these measurements presented overlapping signals due to multiple metal ions, making it challenging to extract accurate information about each metal ion's concentration. To overcome this challenge, we employed Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) analysis. MCR-ALS is a powerful chemometric technique used to separate complex mixture spectra into their pure component spectra and corresponding concentration profiles. [3] By applying MCR-ALS to the obtained UV-Vis spectra, we were able to effectively deconvolute the contributions of each metal ion and obtain the pure component spectra associated with them. The use of MCR-ALS in this project is invaluable as it allows us to unravel the individual contributions of the metal ions, overcoming the spectral overlap and enabling a tentative, but accurate quantification of each analyte and their aggregation with the Ag-nanoparticles.

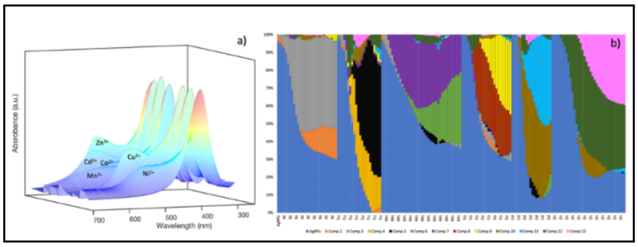

Figure 1: a) surface plasmon absorption bands of functionalized AgNPs titrated with metal ions, b) Distribution of components in the surface plasmon absorption bands (SPABs) obtained by applying MCR-ALS analysis.

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SB-P14

A NEW MOLECULARLY IMPRINTED POLYMER BASED OPTICAL SENSOR FOR LABEL FREE DETECTION OF QUERCETIN

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Quercetin (QU) is a natural flavonoid present in plant-based products, with a wide spectrum of biological functions in the human body including metal-ion chelation, antioxidant, antibacterial and antiviral activities even against *SARS-CoV-2*[1]. This small molecule finds application in prevention therapy of heart diseases, Alzheimer's disease and thalassemia, due to its beneficial health effects such as cardiovascular protection, lipid peroxidation and suppression of proliferation and tumour growth, becoming an important part of human dietary supplements. However, high levels of QU related to unbalanced nutrition or metabolic disorders can produce harmful effects such as kidney damage and suppressed enzymatic activity[2]. For all these reasons, detection and quantification of QU in food and biological fluids is of crucial importance.

Herein, we propose the use of an innovative room temperature vapor-phase synthesis approach to integrate the selective capabilities of molecularly imprinted polymers (MIPs)[3] with the optical properties of nanostructured porous silicon ($nPSiO_2$)[4], used as interferometer, with the goal to develop a robust, highly sensitive and selective optical sensor for QU. To this aim, pyrrole is used as functional monomer leveraging its vapor phase at room temperature and polypyrrole (PPy) thin films embedding target molecules were obtained on the surface of $nPSiO_2$ after 1 hour polymerization. Later, the removal of target from the polymer matrix produced imprinted cavities able to selectively recognize QU. Preliminary detection tests by UV-vis reflectance spectroscopy showed that the sensor can detect QU in aqueous solutions in a dynamic concentration range between 0.5 to 250 µM. Moreover, the sensor selectivity was tested upon exposureto other antioxidant agents such as rutin, gallic acid and vanillic acid recording in each case a higher sensor response for the target molecule. Repeatability and stability tests along with QU detection tests in real matrices are in progress.

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Acknowledgement

This work was partially funded by the European Union Horizon Europe program under grant agreement No 101046946 (RESORB).

SB-P15

GREEN ELECTROSYNTHESIS OF A THIOPHENE-DERIVATIVE BASED MOLECULARLY IMPRINTED POLYMER FOR THE AMPEROMETRIC DETECTION OF TYROSINE

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In human organism the non-essential amino acid tyrosine acts as precursors of neurotransmitters, hormones and pigments[1], with a blood normal concentration in the range 30 – 120 μM, while deficiencies in tyrosine metabolism lead to an increase in blood levels. Among the conventional methods to determine tyrosine concentration, the electrochemical detection represents a valid alternative in terms of sensitivity, accuracy, simplicity and low cost. Molecularly imprinted polymers (MIPs), obtained from the polymerization of a monomer around the target, that, once removed, leaves sites able to specifically rebind the analyte, serve as synthetic receptors enabling to modify the electrodes in order to increase the selectivity of the detection[2].

In this regard, an electrochemical sensor based on a molecularly imprinted polymer was developed for tyrosine detection. The 2,2'-bis(2,2'-bithiophene-5-yl)-3,3'-bibenzothiophene (BT_2-T_4)[3-5] was chosen as functional monomer and MIP electrosynthesis was carried out on screen-printed carbon electrode in ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM TFSI). The very low volumes required (20 μL) and the use of ionic liquid as green solvent represent an environmentally-safe approach for the development of a MIP for tyrosine. Preliminary results of tyrosine amperometric detection showed a linear response in the range 15 – 200 μM. The analytical characterization of the MIP was performed in order to study selectivity, reproducibility, repeatability and stability. Tyrosine amperometric detection was also performed in real samples, such as artificial saliva and human plasma.

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SB-P16

IMPROVING THE SPECIFICITY OF CRISPR-BASED SENSING PLATFORMS USING TRIPLEX-DNA

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The extensive use of CRISPR technology for diagnostic applications has been driven by the discovery of the collateral a-specific cleavage activities of CRISPR type V (Cas12) and type VI (Cas13) systems induced by DNA/RNA binding. In particular, Cas12 is a RNA-guided enzyme that integrate single- and double-stranded DNA target recognition, with signal amplification in one system[1,2]. The collateral cleavage is activated upon binding and is responsible for signal generation, for example, by taking advantage of the Cas12-mediated digestion of single-stranded DNA probes functionalized with a fluorophore-quencher used as fluorescence reporters[3].Here, we describe a strategy for controlling Cas12a cleavage activity by using a rationally designed DNA-based hybridization network based on the formation of Clamp Triplex DNA. Clamp Triplex are DNA probes that can recognize homopurine DNA/RNA target with superior specificity and affinity compared to standard linear or hairpin DNA probe. When a ssDNA target is present, the Clamp Triplex probe alters its conformation that is associated to a reaction network leading to Cas12a activation and fluorescence output. Our molecular design allows us to overcome two hurdles that limit the application of CRISPR-Cas systems in diagnostics: we are able to distinguish with high specificity a single mutation base on the target sequence comprised between 10 and 20 nt by maintain the same LOD of standard CRISPR-Cas12-based detection systems.

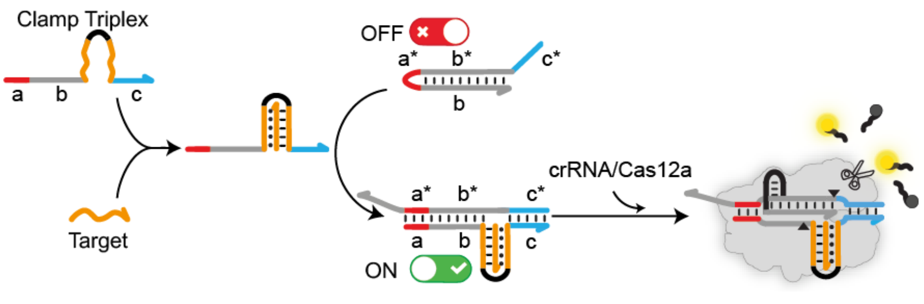

Figure 1. Schematic for controlling Cas12a trans-cleavage activity based on DNA-based hybridization network.

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SB-P17

PAPER-BASED ELECTROCHEMICAL STRIP FOR MONITORING THE EFFICIENCY OF THE ENVIRONMENTALLY FRIENDLY ANTIMICROBIAL COATING

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Paper-based electrochemical (bio)sensors have established a new route in the electrochemical sensing field[1,2], because paper-based electrochemical biosensors have been not only environmentally friendly devices, but recently our group demonstrated further advantages, including the simple combination with vertical microfluidics and their use as a reservoir to deliver smart electrochemical (bio)sensors able to *i) contain the reagents, ii) preconcentrate the target analyte, and iii) synthesize the nanomaterials inside the paper network. Furthermore, these devices have demonstrated their ability to overcome the limitations of the other printed electrochemical sensors in the measurement of entirely liquid samples by detecting the target analyte in the aerosol phase or solid sample, without the additional sampling system*[3]. Herein, we reported the preliminary results obtained within European Project Horizon Europe Reliance for monitoring the efficiency of the environmentally friendly antimicrobial coating using a paper-based electrochemical strip.

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SB-P18

LAB-ON-CHIP BASED ON FLUORESCENT APTASENSOR FOR THE DETECTION OF ZINC AS WATER POLLUTANT

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This work reports the development of a Lab-on-Chip (LoC) system based on a microfluidic network functionalized with a novel aptamer suitable for the recognition of Zn^{2+}, a water pollutant ion, whose high level derives from industrial practices like mining, steel production, coal burning, and burning of waste[1]. The microfluidic network is coupled with an array of amorphous silicon photosensors (a:Si-H) for optical detection and included in a portable system suitable for in-field analysis. The LoC consists of a metallic box containing on the top side of the lid an access hole for inserting a Gilson pipette and in the internal part a light emitting diode (LED). The metallic box includes the electronic board for driving the array of a-Si:H photosensors and the functionalized microfluidic network (Figure 1). The internal walls of the microfluidic channels are functionalized with poly(2-hydroxyethyl methacrylate) (PHEMA) with embedded aptamer having affinity towards Zn^{2+} (Figure 1). In this assay, water solutions of $ZnCl_2$ are flowed into the channels, together with the $[Ru(phen)_2(dppz)]^{2+}$, a DNA intercalating fluorophore. After binding the target, the aptamer forms a folded structure containing a double-strand portion, which in presence of $[Ru(phen)_2(dppz)]^{2+}$ emits a fluorescence signal proportional to the concentration of zinc. The calibration curves obtained using different concentration of $ZnCl_2$ by using the LoC following the assay in Figure 1 and a standard spectrofluorometer using the free aptamer in solution showing a comparable limit of detection of abut 0.1 µM. On the other hand, the sensitivity (slope of the calibration curve) is 0.48 and 0.081 a.u./µM for the on-chip and in-solution measurements, respectively, showing the improved performance of the on-chip assay. These results demonstrate the advantage of the integration of this aptamer assay with microfluidics, while the integration with the a-Si:H photosensor array allows the portability of the system and its use for in-filed analysis.

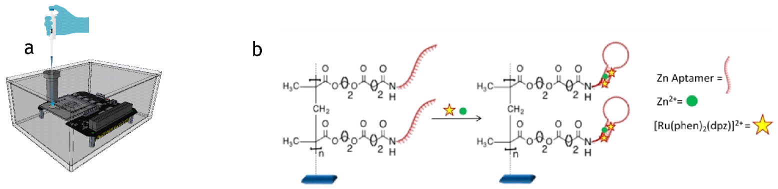

Figure 1: a) Scheme of the lab-on-chip system, b) aptamer based zinc assay.

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SB-P19

A PORTABLE AND ULTRA-SENSITIVE BIOELECTRONIC SENSOR FOR THE SIMULTANEOUS DETECTION OF PROTEIN AND GENETIC PANCREATIC-BILIARY CANCER MARKERS

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The incidence of pancreatic-biliary cancer is estimated at a hundred thousand cases annually. [1] Thus, early detection of pancreatic cancer precursors represents a challenge for clinicians, to apply more effective treatments. The development of new diagnostic methods which can perform highly-sensitive analysis directly in peripheral fluids (liquid biopsy), can be of paramount importance, reducing the invasiveness of surgical resection.[2] The diagnosis accuracy can be further improved through multiplexing analysis, for the detection of multiple cancer precursors simultaneously.[3] This study demonstrates the detection of protein markers of pancreatic mucinous cysts (human Mucin 1, MUC1, and human Complement Decay-accelerating factor, CD55) as well as genetic probes (mutated KRAS sequences) in human serum down to the physical limit (zepto-Molar, 10^{-21} M). An Electrolyte-gated FET-based technology, namely the "Single-Molecule assay with a large Transistor" (SiMoT) platform, was used. The structure was developed in an ELISA-like array, using flexible plastic substrates on which the transistor components were defined.[4] The bio-functionalization procedure of the gold gate surface was assessed independently through Surface Plasmon Resonance (SPR).[5] The simultaneous assay of proteins (MUC1, CD55) and mutated genetic strands ($\text{KRAS}^{\text{G12D}}$) at the single-molecule Limit-Of-Identification, LOI, was demonstrated, paving the way for a new fast and ultra-sensitive screening platform for pancreatic cancer identification.

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SB-P20

DEVELOPMENT OF AN ELECTROCHEMICAL SENSOR BASED ON MIP NANOPARTICLES FOR THE DETERMINATION OF PERFLUOROALKYLS IN WATER

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Perfluoroalkyl substances (PFASs) are synthetic compounds classified as permanent and emerging chemicals. They are also called 'forever chemicals', because the presence of carbon-fluorine functional groups makes them unable to biodegrade naturally, causing them to bioaccumulate in humans and the environment[1]. The design of new monitoring cheap and stable sensors with short response times for the routine quantification of PFAS in situ in water is highly desirable. Molecular imprinting polymers (MIPs) represent synthetic polymeric structures capable of selectively recognising the molecule of interest, such as environmental contaminants, biological target, heavy metal ecc. As such, MIP can be employed in sensors. MIP can be developed in the form of nanoparticles and the production cost of MIP-based sensors is far lower than other analytical instrumentation and they are easy to manufacture and use, even on site. NanoMIPs can be synthesised through various protocols, depending on the nature of the analyte, size and desired shape[2]. In particular, glass beads or silica gels, are used as a solid support and mixed with monomers, cross-linkers and initiators and then polymerised using chemical or photo initiation. In this work, we propose the preparation of a sensor based on nanoMIPs for the determination of perfluorooctanoic acid (PFOA) in water by electrochemical techniques. Nanoparticles were synthesised using the solid-phase protocol[3], immobilised on a screen-printed platinum electrode (SPPtE) by (3-aminopropyl)triethoxysilane (APTES). Dimensional characterization of nanoMIPs by Dynamic Light Scattering (DLS) shows small nanosized imprinted particles (<200 nm) with a polydispersity index (PDI) below 0.3. The sensor was tested towards a wide range of PFOA concentrations (1.5-100 ng/mL) dissolved in PBS (50 mM, pH 7.2) by differential pulse voltammetry (DPV) measurements, showing high sensitivity towards the target.

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SB-P22

TEMPORALLY PROGRAMMED PULSE DNA-BASED REACTIONS

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Many biological processes display a variety of elegant mechanisms that allow their flexible control over time in response to different environmental conditions. Thus the possibility to develop artificial synthetic systems with temporal controlled functionalities can expand our ability to create biomolecular devices and materials with features similar to biological processes[1]. Among these, thanks to the programmability and predictability of DNA-DNA interactions, DNA-based reactions have proved particularly suitable to rationally design temporally programmed synthetic devices[2].
Motivated by the above considerations we developed a strategy to achieve temporally programmed pulse output signals in DNA-based strand-displacement reactions (SDRs)[3,4], one of the most used reaction in the field of DNA nanotechnology that allows to precisely control functional DNA nanodevices. Our approach is based on blocker strands that efficiently inhibit the strand displacement by binding to the toehold domain of the target DNA. Specific enzymatic degradation of the blocker strand subsequently enables SDR, and thus the kinetics of the blocker enzymatic degradation controls the time at which the SDR starts. Then, also the employed input strand, once bound to its target duplex, can be enzymatically degraded over time leading to a pulse output signal. The developed strategy is versatile and can be orthogonally controlled by different enzymes that specifically degrade different blocker strands. Indeed, we designed and established different delayed pulse SDRs using the RNase H and UDG a DNA repair enzymes. Finally, as an application we demonstrate the transient decoration of DNA nanostructures.

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SB-P23

LASER-INDUCED ACTIVATION OF CARBON-BASED INKS FOR (BIO)SENSING PURPOSES

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In the last years, significant efforts have been devoted to develop advanced point-of-care/need electrochemical devices; in this context, conductive inks represent useful and cost-effective tools to fabricate lab-made tailored sensing and electronics. Nevertheless, often pristine inks are characterized by poor electron-transfer ability and electroanalytical features, making them not fully suitable for (bio)sensing purposes. In this framework, the CO_2 laser can result in a useful tool to improve material features and induce nanostructure formation, nevertheless, few efforts have been devoted to using this strategy to improve ink performances [1]. Herein, a CO_2 laser plotter was used to treat commercial graphitic inks, studying the derived electrochemical/electroanalytical effects. At first, the conditions of the laser treatment have been optimized, to maximize the electrochemical performance; the inks, one solvent-based and the other water-based, showed improvement in the electron-transfer ability as a function of the laser power applied. To further characterize the laser-treated inks, the response towards several electro-active molecules, characterized by different reaction mechanisms, was studied; remarkable boosting of the performances was registered for all the probes. Eventually, the potentialities of the laser-activated ink-based transducers were also explored to develop 3rd generation enzymatic biosensors, by using Fructose dehydrogenase. The laser treatment resulted in significant enhancement of the electro-catalytic activity, allowing the ink-based transducers to communicate with the redox enzyme giving rise to significantly enhanced direct electron-transfer event. Despite morpho-chemical characterizations being on-course, these results endorsed the proposed laser approach as a reliable strategy to improve the native electrochemistry of graphitic inks; the hypothesis is that the laser induces a mixed effect, between binders/plasticizers removal and nanostructuration. Therefore, considering the high versatility of screen/stencil-printing to realized ink-based (bio)electronics, the proposed laser-based technology represents a promising route to produce electrochemical (bio)sensors with superior performance.

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Acknowledgements:

This research was funded by the European Union – Next Generation EU. Project Code: ECS00000041; Project CUP: C43C22000380007; Project Title: Innovation, digitalization and sustainability for the diffused economy in Central Italy – VITALITY.

SB-P24

CARBON BLACK AS A COST-EFFECTIVE NANOMODIFIER FOR (ELECTRO)CHEMICAL-FREE PRE-TREATMENT THERMOPLASTIC POLYURETHANE-BASED 3D PRINTED ELECTRODES

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In the past few years, the vision of sustainability has contaminated all sectors, from the economic to the social to the scientific world. Electrochemical sensors have been conceived as sustainable analytical tools due to their low cost, on-site use, no high-power requirements, ease of measurement, and low/no sample processing. In recent years, 3D printed sensors and inexpensive nanomaterials have been developed for smart and environmentally friendly analysis to further increase the environmental compatibility of electrochemical sensors[1]. Here, we report the study of 3D printed electrodes based on thermoplastic polyurethane for electrochemical measurements. To make 3D printed thermoplastic polyurethane-based electrodes suitable for electroanalytical applications, the inexpensive carbon black nanomaterial was used as a filler to improve conductivity and as a nanomodifier of the working electrode surface to improve electrochemical performance[2]. Trough morphological characterization was showed the presence of a homogeneous coating of carbon black with a typical rough and spongy structure. Electrochemical characterization by electrochemical impedance spectroscopy and cyclic voltammetry showed the advantage of using carbon black as a nanomodifier of the working electrode surface after printing, due to the low value of charge transfer resistance and increased peak current intensity. Application as a free chlorine detection tool further demonstrated its applicability for analysis, achieving a linear range between 0.2 and 20 ppm, which corresponds to the maximum allowable value (i.e., 5 ppm) established by the World Health Organization for residual free chlorine in drinking water.

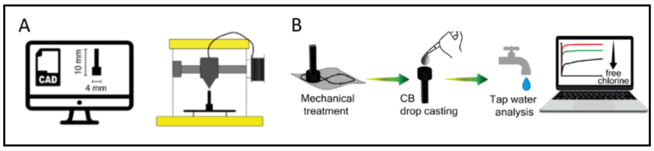

Figure 1: A) Design and fabrication of the 3D printed electrochemical sensor. B) Treatment and modification process of the thermoplastic polyurethane-based 3D printed electrodes for free chlorine detection in tap water.

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Acknowledgment:

Project Water 4.0 n. F/190177/032/X44 funded by Italian Ministry of Economic Development

Poster

Scienze delle Separazioni

SP-P1

AN EASY PROTOCOL BASED ON SOLID PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY FOR THE BIOMONITORING OF PARABENS AND BISPHENOLS IN HUMAN SALIVA

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The development of methods directed toward the assessment of exposure to exogenous agents is of priority importance in addressing the challenges given by chemical exposomics. In this context, this work aimed at developing an easy method for the quantitative determination of parabens and bisphenols in human saliva. Parabens and bisphenols, belonging to the endocrine disrupting compounds, have received considerable attention due to their presence in numerous everyday products[1]. Parabens are used as additives in pharmaceutical products, in personal care products as well as in food and beverage processing while bisphenols are involved in the preparation of epoxy resins, polyvinyl and polycarbonate plastics used to produce medical devices, food containers and kid's toy articles. Biomonitoring is an important tool for assessing the effects of these compounds on humans and their fate in biological systems.

The presented method is based on the combined use of methyl chloroformate as derivatizing agent and solid phase microextraction (SPME) for the extraction of target analytes, followed by gas chromatography-triple quadrupole mass spectrometry (GC-QqQ-MS) analysis in selected reaction monitoring (SRM) acquisition. Using multivariate analysis, different derivatization approaches were compared and optimized, indicating that the use of methyl chloroformate led to better sensitivity than the classical derivatization by acetic anhydride. The optimization of the factors affecting SPME extraction highlighted the good performance of the commercially available overcoated fiber (PDMS/DVB/PDMS) in the sorption process of the derivatized target analytes. Satisfactory results in terms of linearity, limit of quantitation, accuracy, and precision were achieved in the validation procedure of the proposed method. The lower limit of quantitation (LLOQ) values obtained applying the developed method were 10 ng/L for all parabens except for methylparaben and 100 ng/L for methylparaben and all bisphenols. The greenness of the method was evaluated according to the "Green Analytical Procedure Index" (GAPI) and "Analytical greenness metric for sample preparation" (AGREEprep) metrics, demonstrating that our approach is more eco-friendly than the methods already published thanks to the automation of most of the involved operations, minimal sample handing by analyst, and much less quantity of organic reagents (only 20 μl). Based on its characteristics, the presented protocol can be considered a suitable approach to determine parabens and bisphenols in routine analysis for biomonitoring purposes.

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SP-P2

DEVELOPMENT OF AN ANALYTICAL METHOD BASED ON ULTRASOUND ASSISTED EXTRACTION AND HPLC SEPARATION WITH MULTI-WAVELENGTH UV DETECTION OF MULTICLASS POLYPHENOLS IN VEGETABLE BY-PRODUCTS

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Polyphenols are a heterogeneous group of widespread bioactive plant secondary metabolites, comprising simple molecules as well as condensed or polymeric forms that are grouped into several classes according to their chemical structure[1]. The large number of these compounds possessing very different physico-chemical characteristics represents a challenge in the development of efficient multiclass extraction, separation and detection methods[2-5] aimed at the characterization of polyphenolic profiles in different real matrices, in particular those belonging to vegetable by-products that can be used for the development of functional food. In this work a multiclass analysis approach based on a simple ultrasound assisted solid-liquid extraction followed by a HPLC separation with a multi-wavelength UV detection is presented. In the development of the extraction method the effect of important parameters (i.e. time, temperature, acidification, solvent, filter) on both the stability of analytes and recovery have been evaluated. The use of a C18 core–shell column and the development of an efficient multi-step gradient (combination of concave and linear ramps) allowed the separation in less than 21 min of 38 polyphenols belonging to the classes of phenolic acids, flavonoids and other phenols. The determination of polyphenols has been achieved at low ppm levels with recoveries above 80 %. The potential of the proposed method has been also assessed by the analysis of dried vegetable by-products.

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Acknowledgements:
This work was financially supported by the Apulia Region (Italy) through the programme “Aiuti ai programmi integrati promossi da MEDIE IMPRESE ai sensi dell’articolo 26 del Regolamento”, involving CIEMME Alimentari srl and the consulting of the University of Foggia. Project title “Sviluppo di gnocchi arricchiti in ottica sostenibile e ottimizzazione del relativo processo di stabilizzazione” (project code 75BTJR2).

SP-P3

ISOMER SEPARATIONS BY INNOVATIVE GAS CHROMATOGRAPHY STATIONARY PHASES

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The chromatographic separation of aromatic amines and xylenes isomers represents a big issue in chemical and petroleum industries, owing to their high similarity in terms of molecular sizes, polarity, and boiling points: as a result, commercial columns very often do not allow their complete peak separation. For this reason, several typologies of materials with different structures and properties have been developed and proposed as gas chromatography stationary phases in recent years. Macrocycles and ionic liquid-based chain-typed copolymers have emerged, due to their special chromatographic selectivity and separation mechanisms, resulting from their three-dimensional structures and outstanding thermal stability. Very recently, innovative stationary phases based on functionalized calixarene-polyethylene glycol (C4A-mPEG)[1], and amphiphilic triblock copolymer bonded with benzimidazolium ionic liquid (TCP-Bim)[2] were designed, characterized, and used for GC separations of aromatic isomers. The separation features of the C4A-mPEG stationary phase, resulting from multiple molecular recognition processes with analytes, including π-π, H-bonding, dipole-dipole, and van der Waals interactions, allowed to obtain high-resolution performances for a wide range of compounds and their isomers, especially benzaldehydes, phenols, and anilines. Moreover, compared with 4-tertbutyl calix[4]arene (C4A) and polyethylene glycol (PEG) stationary phases, a higher resolving capability was also observed for the separation of toluidine and xylidine isomers. The separation capabilities of the TCP-Bim columns are attributable to different analyte-stationary phase interaction mechanisms, arising from the particular TCP-Bim structure that combines ionic liquid and copolymer peculiarities, showing stronger retention towards aromatic compounds. The high-resolution capabilities of the TCP-Bim column were also tested with different aliphatic cis-/trans-isomers; the excellent separation performances for analytes with very similar properties demonstrated the good potential of these innovative materials as new classes of stationary phases for high-resolution GC separations.

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SP-P4

INNOVATIVE PILLAR[6]ARENE-BASED STATIONARY PHASES FOR HIGH-RESOLUTION GAS CHROMATOGRAPHIC ANALYSES

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In this work, the synthesis, fabrication, and characterization of new stationary phases based on pillar[6]arene derivative modified by long alkyl chains (P6A-C10) for high-resolution gas chromatographic (GC) analyses are reported. Pillar[n]arenes are a new class of macrocyclic hosts that can accommodate specific guests due to their highly symmetrical and rigid pillar architectures with π-electron rich cavities. Quantum chemistry calculations have been performed, showing a difference in non-covalent interactions with the P6A-C10 pillar framework, which leads to specific selectivity for aromatic compounds. The GC columns prepared with these innovative stationary phases exhibited a medium polarity, and good reproducibility for run-to-run, day-to-day, and column-to-column analyses[1], demonstrating great potential as new stationary phases in separation science. Furthermore, peculiar advantages are achieved if compared with the commercial HP-5, HP-35, DB-17, and PEG-20M columns, showing unmatched resolving capabilities toward chloroaniline, bromoaniline, iodoaniline, toluidine, and xylene isomers[2].

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SP-P5

PYROLYSIS ACETYLATION-GC-MS OF POLYETHYLENIMINE SORBENTS FOR CARBON CAPTURE

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Solid sorbents based on silica and polyethyleneimine (PEI) are intensively investigated in the field of carbon capture, utilisation and storage (CCUS). Pyrolysis was proposed to recover the pure silica from exhausted sorbents and convert PEI into potentially useful nitrogen-containing chemical products, such as alkylated pyrazines.[1] However, the knowledge on the chemical composition of the pyrolysate is still limited. Analytical pyrolysis (Py-GC-MS) is a valuable technique to acquire information on chemical structure of pyrolysis products, but the GC behaviour of mono and polyamines can be problematic with non-polar stationary phases. Methylation and silylation are common on-line derivatisation procedures for oxygenated pyrolysis products, but the derivatisation of nitrogen-containing compounds is more challenging. In this contribution, we demonstrate that on-line acetylation of amines can be successfully conducted with acetic anhydride under Py-GC-MS conditions (PyAc). Silica-PEI sorbents, fresh and after use, were subjected to PyAc at 600 °C. Several acetylated methyl, ethyl, ethenyl monoamines and polyamines were revealed conforming previous results and adding novel information on the thermal degradation of PEI. More in general, PyAc shows promises as a novel derivatisation tool in analytical pyrolysis.

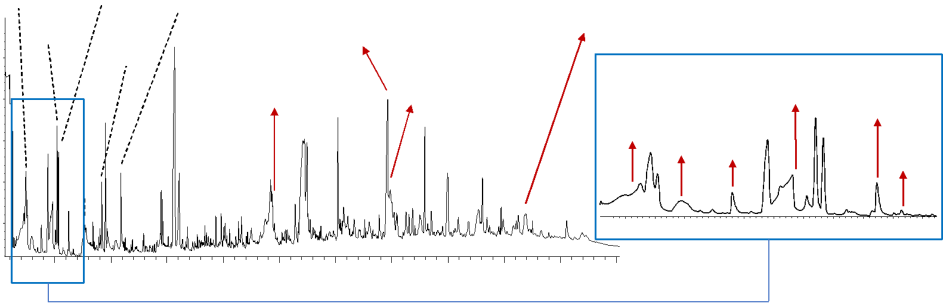

Figure 1: TIC trace from PyAc-GC-MS of mesoporous silica-PEI sorbent

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This work was co-funded by ERANET (H2020) ACT 3 (Accelerating CCUS Technologies, project No. 327334, ABSALT "Accelerating Basic Solid Adsorbent Looping Technology"), the Department of Energy Security and Net Zero (UK), the Ministry of University and Research (IT).

SP-P6

MULTIDIMENSIONAL LIQUID-GAS CHROMATOGRAPHY FOR THE EVALUATION OF MINERAL OIL CONTAMINATION IN *CITRUS* ESSENTIAL OILS

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The present research reports the determination of mineral oil hydrocarbon contamination in *Citrus* essential oils (EOs), using an on-line liquid-gas chromatography system equipped with a lab-constructed Y-interface and a flame ionization detector (FID).

Citrus EOs are increasingly marketed as food flavouring and consumed as food supplements. Over the recent years, there has been significant attention towards the presence of mineral oil hydrocarbons (MOHs) in foods and their potential health risk.

The analysis of MOHs consists in the isolation and separation of the mineral oil saturated hydrocarbons (MOSH) from the mineral oil aromatic hydrocarbons (MOAH), which can be carried out on an LC silica gel column using an *n*-hexane/dichloromethane gradient. Once separated, the two fractions are transferred to a GC-FID system for the quantification purpose.

Eighteen samples were analysed, specifically eleven cold-pressed (CP) and seven distilled EOs. Various degrees of MOSH contamination were detected only in the CP samples, ranging between 10.7 to 338.4 mg kg^{-1} (only one sample was MOSH-free).

Challenges and limitations regarding both MOSH and MOAH analysis will be presented.

Acknowledgements:
The authors gratefully acknowledge the Shimadzu Corporation and Merck Life Science for their support.

SP-P7

HYPHENATED THERMOGRAVIMETRY–GAS CHROMATOGRAPHY–MASS SPECTROMETRY FOR QUANTITATIVE ANALYSIS ON COMPLEX MATERIALS AND THIN FILMS.

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Hyphenated techniques are powerful analytical tools to obtain quantitative analysis from complex systems. In this context, the TGA-GC-MS apparatus allowed the development of reliable and convenient methods. The TGA stage separates according to the temperature of degradation, providing the weight loss. The synchronized GC stage separates the evolved gases emitted at the same temperature. At last, the MS stage provides the identification of each compound contributing to the weight loss. Specific methods were developed to obtain quantitative analyses on ultrathin polymer films,[1] showing a high sensitivity which allows the detection of small differences in composition with minimal amounts of sample. Diethylphosphate-end capped polymers with varying chain length, in bulk and as ultra-thin film were studied,[2] developing, calibrating, and validating a method for the quantification of phosphorus and the determination of repeating units per chain. The technique proved to be very sensitive, flexible, and reliable, maintaining its accuracy over a wide range of sample amount, from bulk to thin layer samples, without needing re-calibration. In the analysis of grafted polymers,[3] an important advantage is that the sample can be introduced as it is, together with its substrate, avoiding inducing structural changes. Moreover, this technique allowed to examine the interlayer composition of hybrid host-guest materials to discern the weight loss due to the organic guest inside the inorganic host versus that of the one adsorbed on the surface, coupling chemical selectivity with topological selectivity.[4-5]

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SP-P8

SIMULTANEOUS DETERMINATION OF ORGANOPHOSPHORUS PESTICIDES AND PHTHALATES IN BABY FOOD SAMPLES BY ULTRASOUND–VORTEX-ASSISTED LIQUID–LIQUID MICROEXTRACTION AND GC–IT/MS

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Baby foods are a soft, liquid paste or an easily chewed food. Some commercial baby foods have been criticized for their contents. This article focuses on the simultaneous determination of organophosphorus pesticides and phthalates by means of a method based on ultrasound–vortex-assisted liquid–liquid microextraction coupled with gas chromatography–ion trap mass spectrometry (GC–IT/MS). The protocol developed allowed the determination of 6 phthalates and 19 organophosphorus pesticides (fig.1) to represent the two classes of compounds, respectively. Freeze-dried product samples (0.1-0.2 g) were dissolved in 10 mL of warm distilled water along with 5 µL of an internal standard (anthracene). Several extraction solvents are tested (fig.2) with n-heptane (250 µL) selected as the suitable solvent for the phthalates determination in similar matrices. Then 1 µL was injected into the GC–IT/ MS system. All analytical parameters investigated are discussed in depth. The best recovery percentage of compounds was between 90% and 110%, at pH 4.0-4.2 and NaCl at 10 g L^{-1}. The method was applied to real commercial freeze-dried samples: significant contaminant concentrations were not found.

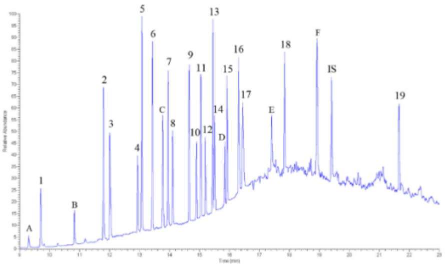

Fig. 1: GC-IT chromatogram of standard

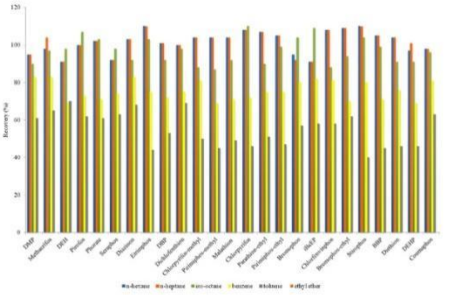

Fig. 2: Recoveries to the different solvents

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ANALYTICAL QUALITY BY DESIGN IN THE DEVELOPMENT OF A SOLVENT-MODIFIED MICELLAR ELECTROKINETIC CHROMATOGRAPHY METHOD FOR THE DETERMINATION OF OMEPRAZOLE AND ITS IMPURITIES

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Impurity profiling constitutes a fundamental part of Quality Control (QC) and consists in the detection and determination of impurities which may be present in a drug substance or a drug product[1]. The aim of this study was to set-up a Capillary Electrophoresis (CE) method for the QC of omeprazole (OME) capsules. OME is a proton pump inhibitor used to treat gastroesophageal reflux disease associated conditions such as heartburn and gastric acid hypersecretion. The method was developed in the Analytical Quality by Design's framework, as recommended by recent ICH guideline Q14[2,3]. According to the Analytical Target Profile, the method should be able to simultaneously quantify OME and seven of its related impurities in the drug product, with specified analytical performances. The selected operative mode was solvent-modified Micellar ElectroKinetic Chromatography (MEKC), based on sodium dodecyl sulfate (SDS) micelles with the addition of *n*-butanol to the background electrolyte (BGE). In the screening phase, a symmetric screening matrix was employed to evaluate the effect of seven critical method parameters on critical method attributes (resolution, analysis time, OME peak width). The critical method parameters included voltage, temperature, BGE pH and concentration, SDS concentration, *n*-butanol concentration, dimethyl-β-cyclodextrin (CyD) concentration. Based on the screening results, the addition of CyD to the BGE was discarded and temperature was fixed at 21 °C. Response Surface Methodology was carried out using an Orthogonal Central Composite Design. The calculated regression models, combined with Monte Carlo simulations, allowed probability maps to be drawn and a Method Operable Design Region (MODR) to be identified. The MODR intervals were defined as follows: borate buffer concentration, 65-80 mM; pH, 9.80-10.20; SDS concentration, 90-110 mM; *n*-butanol concentration, 1.04-1.75 %v/v; voltage, 23-25 kV.

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SP-P10

PRESSURIZED HOT WATER EXTRACTION COUPLED WITH LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY FOR THE FULLY AUTOMATED DETERMINATION OF PHARMACEUTICALS IN SOIL SAMPLES

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In this study, a fully automated method based on pressurized hot water extraction directly coupled with liquid chromatography-tandem mass spectrometry has been developed for the analysis of pharmaceutical compounds in soil samples. For this purpose, a new apparatus for the extraction of solid samples was built, using suitably modified standard chromatographic equipment. The extraction system allows the extractant (i.e., hot water) to be recirculated through a cell, thus allowing to perform an extraction in dynamic mode[1], for the desired number of cycles. The system allows for monitoring the temperature and pressure inside the extraction cell. During the tests, the solvent flow through the system was kept constant at 1 mL/min, while different values of temperature and pressure were tested, in order to evaluate the impact of these variables on the recovery percentage. Based on an univariate approach, the influence of the temperature, pressure, and number of extraction cycles (1, 6, and 12 cycles) on the recovery was evaluated, finding more or less significant effects, depending on the compound investigated. Starting from these results, a multivariate approach was developed, extending the group of target analytes and investigating the aforementioned in wide ranges of values. The main effect was due to the temperature, while pressure and number of extraction cycles exerted a less important influence. Furthermore, the use of aqueous solutions modified with volatile salts (e.g., ammonium acetate) allowed for improving the recovery of some analytes.

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INTENSIFYING DOWNSTREAM PROCESSING OF THERAPEUTIC PEPTIDES THROUGH MULTICOLUMN COUNTERCURRENT PREPARATIVE LIQUID CHROMATOGRAPHY

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Therapeutic peptides are considered one of the most promising class of biopharmaceuticals. Their industrial production (upstream processing) has exceptionally advanced in the last ten years, especially for what regards 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, time and sustainability in the entire production process.
Purification of therapeutic peptides in biopharma industries is usually carried out through single-column preparative liquid chromatography and more chromatographic steps are often required. Indeed, solid-phase synthesis do not lead only to the target peptide but also to a series of product-related impurities which have very similar chemo-physical properties, as well as chromatographic behavior, to that of the target. However, single-column processes suffer of an intrinsic limitation in terms of yield-purity trade-off. This drawback can be practically alleviated through multicolumn countercurrent continuous (or semi-continuous) chromatographic approaches. 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, and solvent consumption is reduced[1,2].
This communication will show, through a series of case studies, the great potential of multicolumn countercurrent platforms to boost the downstream processing of therapeutic peptides. Particular emphasis will be given to Multicolumn Countercurrent Solvent Gradient Purification (MCSGP) technique.

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SP-P12

HYDROGEN AS CARRIER GAS FOR A COST EFFECTIVE PREPARATIVE MULTIDIMENSIONAL GAS CHROMATOGRAPHIC SYSTEM

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The collection of molecules from natural matrices is the goal of each preparative system. Dealing with gas chromatographic (GC) approaches, monodimensional GC analyses for preparative purpose present different limitations. Although wide-bore columns (0.53 mm I.D.) are commonly used, an excess of on-column sample amounts could result in broadened peaks and decreased resolution. This issue may clearly involve in a reduced purity degree, when target analytes needs to be collected for further analytical approaches. Aiming to improve the productivity of the system, a preparative multidimensional GC instrument can guarantee both an improvement of the purity of the analytes isolated, as well as the total collection time [1]. This system is based on a series of Deans switch transfer devices, performing stand-by and cut analyses, aiming to collect target analytes from the end of the capillary column. Dealing with *heart-cut* transfer systems, system configuration is based on additional gas flows (conventionally helium), mandatory for the right performance of each operative mode. In this concern, since the multidimensional preparative system exploits wide-bore columns, higher gas flows are required in each chromatographic dimension, thus resulting in a very high consumption of flowing gas. This issue is even more pronounced when the instrument is exploited to collect milligrams of target analyte, needed, for example, in the case of structural elucidation investigation. Consequently, also due to the renowned increasing cost of helium, this study aimed to find a viable and cost effective alternative. In detail, hydrogen performance was evaluated, by replacing helium both as carrier gas and as additional gas flow for preparative multidimensional GC application.

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Acknowledgements:
We would like to thank Shimadzu Corporation and Merck Life Science for their continuous support

SP-P13

MRM/MS APPROACHES TO INVESTIGATE FEMALE FERTILITY

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Infertility is a global health issue affecting millions of people of reproductive age. According to World Health Organization, available data suggests that globally one in six people experience infertility in their lifetime. Minimally invasive tests for diagnostic purposes are essential in assessing the health status of the male and female reproductive systems. The mainly investigated aspects are related to check the functionality of male and female reproductive system, to predict possible causes of infertility, and to monitor the response of pharmacological stimulation in medically assisted procreation techniques (IVF). The dosage of protein-based fertility hormones in serum samples is a common clinical practice, but their absolute quantification is a great challenge due to biological variability and low serum concentrations. Generally, ELISA assays (enzyme-linked immunosorbent assay) are used in quantifying these molecules. For instance, since 1990, immunological assays like ELISA are implemented in clinical labs for the measurement of serum AMH (anti-Müllerian hormone) by trying to increase the test reproducibility attributed to interference due to the binding of other serum proteins. In present the work, a LC-MS/MS method in multiple reaction monitoring (MRM) has been developed to propose a molecular assay for the quantification of several gonadotropins strictly connected to fertility issues (AMH, LH, FSH and TSH) together with some adipokines, e.g. adiponectin and leptin and its metabolic antagonist ghrelin.The greatest challenge was the set up of the MRM/MS method to quantify AMH due to its low serum concentration (amol). Therefore, Isotope-labelled peptides were used to set up the mass spectrometry method in multiple reaction monitoring ion mode for AMH quantification in serum samples to increase selectivity and sensibility.

Isotope-labelled peptides were used to set up the quantification method for AMH in sera samples. The present study was performed in collaboration with the Merck group warmly interested to set up a new method in alternative to the ELISA assay due to the dosage troubles in terms of reproducibility between the various laboratory kits.

The highly selective approach based on LC-MRM/MS aimed to propose an alternative valid to ELISA tests to quantify in a single run a wide panel of protein hormones crucial to get a more complete understanding of the reproductive health status or to support the progress of pharmacological stimulation in protocols of medically assisted fertilization.

SP-P14

RAPID AND LIMITED-VOLUMNE SOLVENT-EXTRACTION COUPLED TO GC×GC-QQQ MS FOR PESTICIDES DETERMINATION IN CANNABIS PRODUCTS

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The research report a rapid and limited-volume (0.5 mL) solvent-extraction sample preparation process, without any clean-up or pre-concentration steps, for the determination of pesticides in Cannabis Sativa L. products. The analysis of the extracts was carried out through cryogenic modulation comprehensive two-dimensional gas chromatography-triple quadrupole mass spectrometry. The limits of quantification (LoQs) were in the range 0.01-0.5 mg kg^{-1}, the accuracy values (at concentration levels of 0.05 and 0.5 mg kg^{-1}) were in the range between 81.5 and 117.6% with an RSD <11%. Intra-day and inter-day recovery (0.05 and 0.5 mg kg^{-1} concentration levels) were in the 10.9-126.7% and 11.2-126.9% ranges, respectively. Particular attention was devoted to the evaluation of the matrix effect, which was in the range -97.7-184.0%. Among the ten samples subjected to analysis, four of them were found to be contaminated, involving seven pesticides, with most over the regulation residue limits.

Acknowledgements:

The project was funded by the Italian Ministry for the University and Research (MUR) with a "PRIN: PROGETTI DI RICERCA DI RILEVANTE INTERESSE NAZIONALE – Bando 2022" Project n. 202224R9NL "RELIABLE AND RAPID PROFILING OF PESTICIDES IN CANNABIS SATIVA L. BY REAL-TIME IN ELECTRON IONIZATION DETECTION (REI) AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY TECHNIQUES, WITH PARTICULAR EMPHASIS ON THE MINIATURIZATION AND AUTOMATION OF SAMPLE PREPARATION PROCEDURES". The authors gratefully acknowledge the Shimadzu Corporation and Merck Life Science for their continuous support.

SP-P15

DEVELOPMENT AND VALIDATION OF A MULTI-CLASS METHOD FOR THE ANALYSIS OF PESTICIDES IN CEREALS BY COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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Due to the growing trend of organic food, there is a concern about the use of chemicals and pesticides in agriculture. In recent years, several procedures have been validated for the control of pesticides in food. In the present research, a comprehensive two-dimensional liquid chromatography coupled with tandem mass spectrometry is proposed for the first time for a multi-class analysis of 112 pesticides in corn-based products. Notably, a “reduced” QuEChERS-based method as extraction and clean-up procedure prior to the analysis, was successfully employed. Limits of quantification values were lower than the ones fixed by the European legislation; intra-day and inter-day precision were lower than 12.9% and 15.1%, respectively (at the 500 µg/kg concentration levels). Over 70% of the analytes provided recoveries between 70% and 120% range (at 50, 500 and 1000 µg/kg concentration levels) with standard deviation values below 20%. In addition, matrix effect values were in the range between 13% to 161%. The method was applied to the analysis of real samples, and three pesticides were detected at trace levels in both samples. The findings of this work pave the way for the assessment of novel quality control procedures to be employed for the quantification of target contaminants in complex matrices such as corn products.

Acknowledgment:

The researches were performed within the framework of the Research Project PRIN 2017: At the forefront of Analytical ChemisTry: disrUptive detection technoLogies to improve food safety – ACTUaL, supported by the Italian Ministry of University and Scientific Research, no. Prot. 2017RHX2E4.

SP-16

MULTI-PESTICIDE RESIDUES DETERMINATION IN HEMP INFLORESCENCES USING A “SCALED” QuEChERS AND FM GC×GC-QqQMS

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An analytical method for the determination of multi-pesticide residues (54 target analytes) in Hemp Inflorescences by using a “scaled” QuEChERS extraction method and flow-modulated comprehensive two-dimensional gas chromatography-triple quadrupole mass spectrometry was performed.

The samples were prepared according to the QuEChERS procedure as reported by the official European Union method, namely EN 15662:2018. Briefly, 1 g of vegetable product was grinded, extracted with 3 mL of acetonitrile and Supel QuE Citrate, and then subjected to the clean-up procedure using 3 g of Supel QuE PSA. Leading to a reduction of *circa* the 70% of solvents and sorbent materials.

The gas chromatographic separation was optimized by using a relative high flow (8 mL) in the second dimension. The modulation period was of 4.5 sec with a reinjection period of 450 msec.

The limits of detection, and limits of quantification for all the analytes were calculated.

Acknowledgements:

The project was funded by the Italian Ministry for the University and Research (MUR) with a “PRIN: PROGETTI DI RICERCA DI RILEVANTE INTERESSE NAZIONALE – Bando 2022” Project n. 202224R9NL “RELIABLE AND RAPID PROFILING OF PESTICIDES IN CANNABIS SATIVA L. BY REAL-TIME IN ELECTRON IONIZATION DETECTION (REI) AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY TECHNIQUES, WITH PARTICULAR EMPHASIS ON THE MINIATURIZATION AND AUTOMATION OF SAMPLE PREPARATION PROCEDURES”.

The authors gratefully acknowledge the Shimadzu Corporation and Merck Life Science for their continuous support.

Poster

Bioanalitica e Omics

B-P1

ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-ION MOBILITY-HIGH RESOLUTION MASS SPECTROMETRY METABOLOMICS FOR CEREAL QUALITY

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Advanced data acquisition modes in high resolution-MS permit a comprehensive profiling of food samples, representing a valuable tool to study the metabolic changes developed by organisms in presence of external factors. In the present study, ultra-high performance liquid chromatography-ion mobility-high resolution mass spectrometry (UPLC-IM-HRMS) combined with chemometrics was applied to evaluate the metabolic response to different sustainable treatments in wheat grain of *Triticum durum* (cultivar Svevo) grown in 2020 and 2021. The use of a Synapt-G2-Si HDMS hybrid quadrupole/ time-of-flight mass spectrometer in both positive and negative modes enabled to acquire a comprehensive metabolite profiling of wheat grain associated to four agro-sustainable treatments, i.e., control, biochar addition, commercial biostimulant addition and the combined biochar-commercial biostimulant treatment. Elevated energy (MS^E) data independent acquisition mode allowed for the simultaneous acquisition of HR spectra related to both the precursor and fragment ions within a single chromatographic run[1]. To reduce the high number of features, filtering and data reduction strategies in terms of intra-group variability, minimum fold change and statistical power were used. A supervised Partial Least Square-Discriminant Analysis pattern recognition approach was applied: by selecting six latent variables a good discrimination among the treatments was feasible with good performance in both fitting and cross-validation. According to the VIP score criteria > 2, 265 and 285 metabolites for Svevo 2020 and Svevo 2021 cultivars, respectively were submitted to identification considering the information deriving from accurate mass measurements, fragmentation studies, analysis of the isotopic pattern, library matching, score fit and collisional cross section values. A total of 88 and 45 metabolites were identified in samples harvested in 2021 and 2020, respectively among which metabolites belonging to carbohydrates, amino acids, fatty acyls, flavones, flavonoids, glycerophospholipids and glycolipids, being the up-regulation of lipids particularly affected by the combination of biochar-commercial biostimulant treatment.

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DETERMINATION OF OXIDATIVE STRESS MARKERS IN ORAL FLUIDS BY SPE-DLLME AND UPLC-ESI-MS/MS ANALYSIS

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The term oxidative stress (OS) describes a condition where oxidizing species exert their toxic action, usually due to a lack of adequate protective mechanisms or to an overproduction of oxidizing agents and it is involved in aging processes and in many cardiovascular diseases, diabetes, and carcinogenic processes[1]. It is therefore evident that robust and reliable biomarkers for OS identification represent a crucial aspect to investigate the role of OS in health and disease. Many studies have demonstrated the correlation between the levels of lipid peroxidation products and pathological states, and consequently their use as biomarkers for the early diagnosis and prognosis of diseases[2]. Isoprostanes (IsoPs) have been evaluated over the years as possible biomarkers, given their strong correlation with systemic OS levels. A disadvantage for IsoPs can be that the oxidation of arachidonic acid competes with many other reactions to give numerous products, which makes the concentration of IsoPs very low and the matrix effect should be considered during mass spectrometry analysis, in particular when dealing with electrospray ionization[3]. Different matrices can be used for the evaluation of IsoPs for the determination of OS, usually urine and plasma. Anyway, other matrices could be considered for the OS measurement. Saliva, and in general oral fluid (OF), has demonstrated to be an interesting matrix due to the easy sampling and the good correlation with plasma.The presented method proposes an analytical protocol for the extraction and quantification of 5 different IsoPs from OF. In particular, the combination of two different sample preparation techniques, Solid Phase Extraction (SPE) and dispersive Liquid-Liquid Micro Extraction (dLLME), were used for the extraction and clean-up and applied for the first time on this class of molecules. This combination led to high enrichment factor, providing high sensitivity, together with the suppression of matrix effect. The proposed procedure showed a 20 fold enrichment factor, allowing the detection of the target compounds at very low levels. The selectivity and sensitivity of the whole analytical procedure allowed to detect IsoPs with high confidence in real samples.

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B-P3

QUANTITATIVE DETERMINATION OF A NEW N-ACYLETHANOLAMIDE DERIVATIVES IN BIOLOGICAL SAMPLES

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As well known, in order to counteract neuropathic pain, such as fibromyalgia disease, human body alters the balance by the endocannabinoid system. In particular, these disorders involve molecules called *N-Acetyl Ethanol Amides*, such as Palmitoylethanolamide (PEA), Arachidonyl Ethanolamide (AEA), Oleylethanolamide (OEA), which directly or indirectly act on the endocannabinoid system to counteract neuroinflammatory and painful processes[1].

NAEs quantification in biological matrix is an analytical challenge, due to their chemical features, complex extraction from matrices and their low concentration in human tissue[2]. Therefore, we are using an HPLC MS/MS method to quantify endocannabinoids in human tissues, including brain, liver, urine, etc.

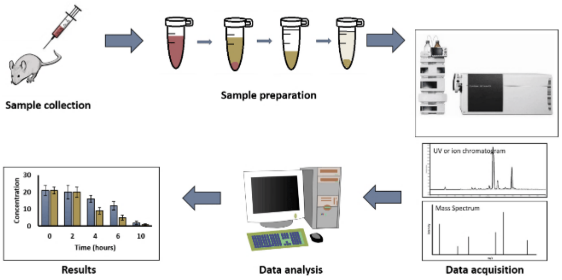

Figure 1: Analytical method scheme.

In this work a comparison between *Solid Phase Extraction* (SPE) with the *SPE-Online Extraction* technique and *Liquid - Liquid Extraction* (LLE) was carried out.

In particular, *Epitech Group SpA* developed 2-pentadecyl-2-oxazoline (PEA-OXA) as a *pro-drug* to oppose fibromyalgia symptoms.[3] PEA-OXA isotope with four C^{13} atoms, as isotopic internal standard, was synthesised for the purpose. The synthesis was performed in anhydrous toluene, using 3 Å molecular sieves and CaO. Subsequently, a chromatographic method was developed to quantify the concentration of the new product PEA-OXA after administration in both mouse and human experimental groups.

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We would like to thank ProTIDol (PO-FESR Sicilia 2014/20) n. 08ME2110000209 for financial support.

A WORKFLOW FOR METABOLOMIC ANALYSIS OF HEAT-STRESSED LEAVES

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Grapevine (*Vitis* spp.) is the most extensively cultivated fruit crop in the world and its economic importance is mainly related to wine production[1]. In recent years, the increased frequency of extreme phenomena such as heat waves has been recognized as one of the most significant climate factors negatively affecting grape yield and berry composition, with tremendous consequences on wine quality[2]. Therefore, studying the metabolic and genetic factors that are involved in grapevine response to high temperatures is essential to gain knowledge on thermotolerance mechanisms, with the final aim of improving vineyard management strategies and plant breeding programs. However, literature on plants resilience to heat stress is scarce and usually focuses on selected metabolites, mainly related to oxidative stress, with a targeted approach[3]. Here, we report the development of a metabolomic workflow, from sample collection and extraction to sample analysis and data interpretation, for a preliminary evaluation of leaf metabolome alterations due to stress factors. In particular, the behaviour of selected grapevine plants during hot days was studied by analysing their volatile organic compounds (VOCs) profile by means of headspace-solid phase microextraction (SPME) GC-MS technique. Together with this well-known protocol, the metabolite modulation under high temperatures was investigated with a HPLC-HR-ESI-MS method under different chromatographic approaches, using conventional C18 and weak anionic/cationic mixed exchange stationary phases. This evaluation provided a first wide screening of both primary and secondary metabolites, suggesting the weak cation-exchange mixed mode column as the best compromise for this metabolic fingerprint. A comparison between full-scan, data dependent (DDA) and data independent (DIA) acquisition modes was also performed to select the best approach for our metabolomic application. To this purpose, data processing was carried out with two different software: MS-DIAL 4.9 and an R package "xcms". Preliminary results obtained from the first two years of study will be presented.

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This work is supported by the PhD project 'Dissecting the genetic and physiological mechanisms of grapevine resilience to heat stress' (C3A-UniTN, FEM, UniPD)

A DIA-PROTEOMICS STRATEGY AS SUPPORT FOR THE SCREENING OF SMALL-MOLECULE MODULATORS OF HISTONE PTMS

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Post-translational modifications (PTMs) of histones include chemical alterations that occur on histone proteins after their synthesis, involving the addition or removal of chemical groups such as acetyl, methyl, phosphoryl, ubiquitin, SUMO, and others to specific amino acid residues. These modifications play a critical role in regulating chromatin structure and function, influencing DNA packaging and gene expression. Mass spectrometry (MS) has been used to quantify histone PTMs for two decades. However, recent advances have significantly improved the ease, speed, and reproducibility of the method[1]. This study aimed to explore the impact of a small library of heterocyclic compounds on the levels of histone PTMs in human colon cancer cells. For this purpose, we applied a label free bottom-up proteomics approach to identify and quantify main PTMs of histones H3 and H4. Cancer cells were incubated with investigated compounds, and the isolated histones were digested with trypsin. However, use of trypsin on histones results in peptides that are too short to retain on reversed phase chromatography columns and a lack of charge density, making them not amenable for MS. Thus, propionic anhydride derivatization of free amine groups on the N termini and lysines before a trypsin cleavage was applied. Finally, samples were desalted using C18 and HyperSep™ SpinTip and analysed using a nano-HPLC coupled online with an Orbitrap Fusion MS. Data were acquired using a data-independent (DIA) acquisition method, consisting of a full scan MS spectrum performed in the Orbitrap, followed by 16 MS/MS using HCD fragmentation and detected in the ion trap. DIA data were searched using EpiProfile 2.0[2]. Our results showed that thiobarbiturate derivatives reduced, even if with different potency, the acetylation level of histones H3 and H4.

In conclusion, the proteomic approach employed in the analysis of PTMs plays a crucial role in unravelling the intricate and dynamic nature of these modifications. It provides valuable insights into protein function, cellular signalling, and disease mechanisms, contributing to a deeper understanding of how PTMs regulate biological processes.

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B-P7

USING WASTEWATER TREATMENT PLANTS TO KEEP AN EYE ON PUBLIC HEALTH: AN INTERDISCIPLINARY STUDY ON BIOAEROSOL AND WATER SAMPLES

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The continuous emergence and spread of antimicrobial resistance (AMR) pose significant challenges to public health. Wastewater treatment plants (WWTPs) have the potential to function as pivotal monitoring locations for the surveillance of antibiotic resistance in bacteria. WWTPs can be regarded as a reservoir of chemical and microbiological data pertaining to determinants of community health. As such, they offer a glimpse into the chemical and microbial profile of the population.

A short pilot study, conducted at the Servola WWTP (Trieste, NE Italy, serving the equivalent of 190000 inhabitants) investigates the application of advanced bioaerosol and water sampling techniques in WWTP in a comparative analysis, highlighting the strengths and limitations of each approach[1]. The results provide valuable insights into enhancing the effectiveness of sampling techniques for the detection of aerosolized microorganisms and pharmaceuticals in wastewater, thereby improving their accuracy and efficiency. The integration of sound preprocessing, Orbitrap mass spectrometry[2], and Illumina shotgun metagenomics analysis[3] provides a powerful tool for monitoring public health indicators, including AMR prevalence and pharmaceutical pollution. By examining untreated water and aerosol particles, this research sheds light on the potential transmission pathways and risks associated with antibiotic-resistant bacteria.

This interdisciplinary approach will enable the setup of an operational pipeline for comprehensive monitoring of aerosolized microbes, antibiotic resistance genes, and pharmaceuticals, thereby aiding in the development of targeted interventions and strategies to mitigate the impact of these factors on public health.

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FT-IR SPECTYROSCOPIC ANALYSIS IN TANDEN WITH CHEMOMETRIC TOOLS FOR THE CHARACTERIZATION OF CECAL CONTENT OF MICE: EFFECTS OF HIGH FAT DIET

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Metabolite profiles associated with the gut microbiota offer valuable insights into the influence of lifestyle and dietary factors on both health and diseases both in animal models and in humans. In recent years, infrared spectroscopy has been demonstrated to be a valuable tool to investigate fecal and cecal content.[1-4] This study focuses on investigating the metabolite composition of mice cecal content using a fast and novel Fourier-transform infrared spectroscopy (FT-IR) method that involves the deposition of samples onto polypropylene sheets, enabling efficient analysis and characterization of metabolites and offering advantages such as requiring small sample quantities and minimal preparation steps.[5] Preliminary results of principal component analysis (PCA) of the FT-IR spectra demonstrate the feasibility and efficiency of the method to characterize low molecular weight (LMW) metabolites and biomolecules in mice cecal content. Distinctive spectral features corresponding to various metabolites were observed in four groups of mice reared for 10 weeks in the following conditions: they were fed with standard diet (19% proteins, 6% fibers, 7% minerals and vitamins moisture, 64% carbohydrates and 4% fats), high-fat diet (26% proteins, 6 % fibers, 7% minerals and vitamins moisture, 26% carbohydrates and 35% fats); standard diet + 0.23% beer; high-fat diet + 0.23% beer)**.** Our findings suggest diet-induced variations in the high and low molecular weight metabolite profiles and showcase the potential of the developed method for studying the impact of diet on gut metabolism. Further analysis and the interpretation of FT-IR spectra will be conducted using also other complementary techniques to identify specific metabolites and elucidate their variations among the different diet groups. FT-IR method with the deposition on polypropylene sheets provides a valuable tool for the efficient, low-cost, and reliable characterization of cecal content metabolites, eventually contributing to the understanding of the effects of healthy lifestyles on gut composition and metabolism.

B-P7

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Poster

Forense, Tossicologia e Salute

FT-P1

DEVELOPMENT OF A CONFIRMATION METHOD FOR THE THC CONSUMPTION BY UPLC-MS/MS

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Cannabis sativa L. is a plant species of Cannabis. In addition to its recreational use as a drug of abuse, the plant has widespread alternative uses including the production of food, cosmetics (hemp), textiles and medicinal application[1]. In the early 1980s a series of studies began on the possibility of determining substances of abuse in the keratin matrix depending on their lipophilicity, molecular weight, pKa and steric bulk in a stable manner over time. The analysis of substances of abuse in keratin matrix is an ideal addendum to the analysis of blood or urine. When toxicology laboratories are required to investigate past exposure to cannabis, analysis of hair can provide powerful evidence. In particular, the target compounds in hair analysis are: Δ(9)-tetrahydrocannabinol (THC), the main psychoactive compound of cannabis and its metabolite 11-nor-9-carboxy-Δ9-THC (THC-COOH)[2]. Usually, after ingestion, traces of substances and their metabolites are deposited into hair via the bloodstream and into the growing follicle. Quality assurance is a major issue in drug testing in hair resulting in strict recommendations, validation procedures or inter-laboratory comparisons. Furthermore, recent trends in research concerning hair analysis are discussed due to the low concentration of legislative limit of THC-COOH (2pg/mg) as well as novel analytical procedures. The aim of this work focuses on basic aspects of method development and validation of hair testing procedures, in particular a SPE clean-up protocol was developed following Standard Practices for Method Validation in Forensic Toxicology (SWGTOX) guideline, in order to eliminate possible interfering compound and avoid the matrix effect in sample analysis considering the necessary enrichment factor to reach low limit of quantification.

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FT-P2

MAGNETIC SOLID PHASE EXTRACTION FOR THE SIMULTANEOUS DETERMINATION OF 50 DRUGS OF ABUSE IN HAIR BY MEANS OF UHPLC-MS/MS ANALYSIS

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The increasing phenomenon of drug addiction and the introduction of New Psychoactive Substances (NPS) have led to a progressive growth of research in the field of forensic analytical toxicology[1]. For this reason, it is crucial to develop effective analytical protocol to assess drug assumption. Hair testing has gained attention in this contest since it is a unique material for the retrospective detection of drugs, due to its large detection window.

In this work, a multiclass method for the simultaneous identification and quantification of fifty drugs of abuse belonging to different chemical classes in hair is proposed. A simple extraction followed by a fast, unexpensive and green clean-up is showed, while the analysis is performed by means of UHPLC-MS/MS.

Substance were extracted from decontaminated and pulverized hair by means of a solution of MeOH:MeCN:Acetate buffer pH 5.3. Thus, clean-up was performed by means of dispersive magnetic solid phase extraction (m-SPE) allowing a fast and selective extraction. In this case, Fe_3O_4-SiO_2-C18 nanoparticles were synthetized and characterized by means of FT-IR, DLS and SEM [2]. Thanks to the magnetic core, every step of the clean-up is regulated by the use of an external magnetic field, so the procedure is fast and requires a minimal sample manipulation. The extract of the elution step is directly injected in the UHPLC-MS/MS system. In this case a scheduled Multi Reaction Monitoring acquisition method was developed, allowing the monitoring of more than 150 targeted MRM transition.

Preliminary results showed good extraction recoveries, higher than 50% for all the analytes; LODs and LOQs are compatible with national and international cut-off values and are all in the order of pg mg^{-1} of hair. Also, the possibility to reuse the same particles up to four times were tested and results shows the absence of any carry-over or particles contamination, highlighting the unexpensive feature of the protocol.

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STABILITY STUDIES OF TOBRAMYCIN USING A VALIDATED HPLC-DAD METHOD WITHOUT DERIVATIZATION

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Most assays have been developed for the determination of Tobramycin (Tbm), an aminoglycoside antibiotic, in pharmaceutical formulations. Several analytical methods reported in the literature are based on tobramycin derivatization for its quantification.

So starting from literature data and our knowledge, we developed a method for Tbm determination using a HILIC as stationary phase, obtaining good results following International Guidelines, in terms of calibration, precision (intra and inter-day), selectivity, LOQ, and LOD. Another interesting shrewdness is that it is a few minutes course with the isocratic flow and percentage of mobile phase, which are easy to prepare and compatible with MS/MS. The choice of mobile phase comes from the large use of instrumentation as LC-MS/MS about Tbm.

The performance of the developed analytical method was evaluated on study of Tbm stability in different buffers, for example, phosphate buffer, HEPES, MES, and water, finding some interesting singular typicality. The Tbm stability was carried out at different temperatures, 25, 37, and 70°C, starting from room temperature and arriving at extremely conditions.

This validated method can be used to detect Tbm in pharmaceutical formulations, for pharmacokinetics study, to determine its entrapment efficiency and release from drug delivery systems.

In conclusion, the HPLC method without involving Tbm derivatization follows the principles of Green Analytical Chemistry (GAC), because the solvents used for Tbm derivatization are dangerous and toxic.

FT-P4

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN INDOOR WORKING ENVIRONMENTS BY HEAD SPACE SOLID PHASE MICROEXTRACTION GAS CHROMATOGRAPHY - MASS SPECTROMETRY ANALYSIS

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Volatile Organic Compounds (VOCs) are emitted into the atmosphere from natural and anthropogenic sources; therefore, it is critical to study these compounds and monitor them by developing reliable and effective methods[1,2]. In this work, an untargeted volatolomic approach is proposed for the evaluation of the exposure to volatile organic compounds of workers in an engine manufacturing plant in Southern Italy. Indoor working environment conditions were studied in different areas and in different work stages, to assess the respective risks. Occupational exposure to VOCs was evaluated by GC-MS measurements coupled with Head-Space Solid-Phase Microextraction (HS-SPME). The analytical procedure was optimized in terms of SPME fiber, adsorption time, desorption time, and temperature gradient. For the microextraction of VOCs, the SPME fibers were exposed to the headspace in two different areas of the manufacturing factory, *i.e.,* in the mixing painting chamber and the engine painting area. Moreover, the sampling was carried out with the painting system active and running (system on) and with the painting system switched off (system off). Overall, a total of 212 compounds were identified, but only 17 compounds were always present, in both zones (mixing painting chamber and engine painting area), regardless of system conditions (on or off). Finally, a semi-quantitative evaluation was performed considering the peak area value of the potentially most toxic compounds by multivariate data analyses (ANOVA and Principal Component Analysis) to explore differences in the VOC composition.

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FT-P5

WATER POLLUTANT TRANSFORMATION PRODUCTS STABILITY AND CELL TOXICITY

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Over the last decades, the worldwide environmental pollution rapidly increased. In 2013 the European Council established a water pollutant watch list annotating all the new possibly hazardous molecules. Numerous studies attempted to establish a connection between water pollution and environmental damage[1], but only a few of them focused on human health. The aim of our study was to develop an analytical and a biomolecular approach to assess the human health risk connected to the presence of emerging pharmaceutical pollutants in aqueous environment. We selected three drugs: ofloxacin and ciprofloxacin, two fluoroquinolones antibiotic, and diclofenac, one of the most common Non-steroidal anti-inflammatory drugs (NSAID) worldwide. A recent study identified these compounds in the majority of world rives[2]. Despite the metabolism of these drugs is well known, and their transformations in the environment were previously studied[3,4], the human toxicity of their transformation products (TPs) remains an open question. After the confirmation of the described TPs using heterogeneous TiO_2 mediated photocatalysis, we assessed their stability at room temperature (RT), at -20°C and 37°C with the developed high performance liquid chromatography coupled to high resolution mass spectrometry (HPLC-HRMS) methodology. The results showed that freezing did not increase the stability of TPs. Once assessed the stability of the TPs, we evaluated the toxicity of parent compounds and TPs in two human pulmonary epithelial cell lines (both normal and oncogenic, i.e., BEAS 2B and BEAS 2B KRAS G12C) for three days at 37°C. The data showed that the TPs formed after 5 minutes of irradiation were more toxic than the precursor compounds. The viability of the cells decreased to reach less than 5% at the higher concentration (5 mg/L). In conclusion, preliminary results indicated that TPs derived from high concentration of photocatalyzed drugs can be toxic for human pulmonary cells.

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FT-P6

RELASE STUDIES OF BACTERIOSTATIC COMPOUNDS WITH A MULTIRESPONSIVE DRUG DELIVERY SYSTEM

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Antibiotic resistance is a huge problem for the effective treatment of infectious diseases. While a considerable number of new anti-infective agents have been developed by modifying existing structures, the same cannot be said for new classes of antibiotics. Despite efforts in various research areas, the fight against antimicrobial resistance remains an ongoing effort, primarily due to the continuous adaptation of pathogens through various strategies[1]. A new drug delivery approach has offered new hope for overcoming antibacterial resistance. Novel drug delivery systems[2] include polymeric nanoparticles, liposomes, metal nanoparticles, dendrimers and lipid-based nanoparticles, which are effective against severe microbial infections and in combating antimicrobial resistance. Most of the active pharmaceutical compounds developed today have hydrophobic groups and ionizable functions, while solubility in water is an extremely variable parameter. This issue is addressed by carefully selecting systems for the delivery of such drugs as biodegradable and biocompatible polymers[3] with chemically analogous characteristics.

Here we report the method for the analytical determination of the degree of loading of molecules with antimicrobial activity delivered by polymer-based nanostructures of hydrolyzed Styrene Maleic Anhydride (hSMA). Berberine (a natural alkaloid with bacteriostatic activity) and the synthetic analog NR16 were chosen to be delivered by the above lipid-polymer system. Model systems were then built to study and modulate the release of the molecules with antibacterial activities under various conditions simulating real ones.

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Acknowledgements:

We would like to thank the INF-ACT Foundation and PNRR PE 13 *"One Health Basic and Translational Research Actions addressing Unmet Needs on Emerging Infectious Diseases*" for financial support.

FT-P7

SKIN ABSORPTION OF POTENTIAL TOXIC METALS FOLLOWING EXPOSURE TO URBAN DUST

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Urban dust is a mixture of particles suspended in the atmosphere. Their sources include factories, home heating, power plants, waste incinerators, combustion engines, construction activities, fires, natural windblown dust, etc. Major components of particulate matter (PM) are metals, organic compounds, materials of biologic origin, ions, and carbon-based particles. Recently, it has been reported that PM is associated with increased risks of skin diseases, especially atopic dermatitis in children[1].

The skin constitutes a protective barrier to external physical and chemical aggression. Although it is generally considered poorly permeable to xenobiotics, it has been demonstrated that skin represent an entry route for metal ions. Metals may penetrate inside the skin inducing more or less local effects such as skin sensitization (Ni, Cr, Co) and potential metals diffusion into the circulatory system. The aim of this study was to investigate the percutaneous penetration of potential toxic metals (Pb, As, Cd, Cr, Ni, etc.) following exposure to urban dust using the Franz diffusion cell method.

The urban dust (Standard Reference Material 1649b, NIST) dispersed in synthetic sweat (1%w/v) has been applied to intact as well damaged skin for a 24-hour exposure period. Receiving phases and skin tissues has been collected and analysed by Inductively Coupled Plasma – Mass Spectrometry for the quantification of potential toxic metals.

The present study demonstrates that, after the application of urban dust on the skin surface, some metals, and in particular the hazardous Pb, As, Ni and Cd, can penetrate the dermal layers and permeate into the receiving phase. Moreover, absorption through damaged skin is significantly higher than through intact skin, as a result of the weaker cutaneous barrier function.

These results confirm those of a previous study that evaluated the skin absorption of metals after exposure to road dust[2] and suggest that dermal absorption of metals could be relevant in environmental exposure scenarios.

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COMPARISON AND VALIDATION OF ANALYTICAL METHODS FOR TRACE ELEMENTS DETERMINATION IN BIOLOGICAL FLUIDS

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The World Health Organization (WHO) defines human health as a state of complete physical, mental, and social well-being. Considering the evolution of the concept of the environment which, indicates the network of relationships between living communities today, including humans and the environment, the environment-health combination can be considered inseparable. Environmental pollution is now a widespread phenomenon: exposure to natural (*e.g.*, transgenic foods and viruses), physical (*e.g.,* ionizing, and non-ionizing radiation), and chemical agents (*e.g.*, heavy metals, pesticides, dioxins) present in the environment can give rise to bioaccumulation processes, causing considerable damage in them, and in the most severe cases lead to death[1]. As for the inorganic pollutants, arsenic, cadmium, chromium, mercury, and lead[2] and some nitrogen, phosphorus, and oxygen compounds should be mentioned. Men and their state of health can be considered essential indicators of the environmental state, evaluating the presence of contaminants within biological matrices. Each biological matrix retains a different pollution trace capable of being conserved for variable times[3]. In particular, urine matrix represents the biological matrices of choice for clinical and forensic investigations[4]. This is "stable" matrix since it has less variability than other matrices, for example, nails and hair, which are subject to various sources of external contamination. The main objective of this project is the validation of an analytical method for the determination of trace elements (Hg, Li, Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Sn, Sb, Te, Ba, Pb, U) in human urine, using the method described by ISTISAN Report 15/30 as a starting point and reference and the subsequent instrumental determination by inductively coupled plasma mass spectrometry, ICP-MS[5,6]. Regarding the treatment of the samples, two different procedures were compared: oxidative acid digestion assisted by microwaves and acid dilution. The performance obtained by the latter meets the requirements necessary for the validation of a method, according to Eurachem Guideline "Fitness for Purpose of Analytical Methods"[7]. In conclusion, both validated methods proved to be fast and efficient and will be applied to different case studies characterizing projects that aim to correlate the environmental impact on the human body.

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SELECTIVE DETERMINATION OF METHYLMERCURY IN HUMAN HAIR BY A SIMPLE ICP-MS BASED METHOD

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Mercury species constitute a significant hazard to all life forms within the biosphere. The way different forms of Hg interact with the environment, their ability to be absorbed/accumulated by living organisms, and their impact on human health are species-specific. In fact, methylmercury (MeHg) has a higher toxicity and tendency to bioaccumulate than inorganic species (iHg): these aspects make fish consumption (especially of species at the top of the food chain) a critical path of exposure to MeHg and, consequently, a global public health risk. The monitoring of exposure to MeHg in fish consumers is generally done by measuring MeHg (or total Hg) concentration in blood (biomarker). Recent studies proved that MeHg tends to accumulate in human hair reaching concentrations up to 250 times higher than in blood making hair a valuable and less invasive alternative biomarker of MeHg exposure: MeHg concentrations ranging from tens of µg/kg to a few mg/kg can be found in human hair according to the individual eating habits. In this context, exposure monitoring calls for the development of highly selective and sensitive analytical speciation methods to meet the requirements imposed by this specific application. We recently demonstrated the potentialities of a simple speciation method based on ICP-MS to determine MeHg selectively and rapidly in biological samples (fish tissue and plankton)[1] by blocking iHg species in a short home-made column filled with a strong anion exchange resin placed in front of the ICP nebulizer. The developed analytical protocol, however, involves a dilution step after Hg species extraction hindering the analysis of very low concentrated samples. As an advancement, we have developed a new extraction/elution media to avoid the dilution step: an optimized HCl-HBr-thiourea mixture was used and directly analyzed after a 15-minutes long ultrasound-assisted extraction. MeHg is determined in 100 seconds with a limit of detection of ~ 6 $\mu g\ kg^{-1}$ in solid samples (based on a 20 mg sample mass) and negligible iHg interference: iHg:MeHg ratios up to 50 (an uncommon case for human hair samples) are well tolerated under optimized conditions. The overall procedure was validated by standard reference materials of human hair (NIMD-01). Then, the proposed method was applied to 55 human hair samples finding a very good correlation between MeHg concentration and the individual weekly intake of fish and seafood. These findings testify the capabilities of this low-cost and easily implementable method for high-throughput MeHg exposure monitoring.

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FT-P10

IN VITRO SKIN PERMEATION OF METALS FROM COSMETIC PRODUCTS

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Cosmetic products are widely used all over the world. The term "cosmetics" includes many kinds of products. Decorative cosmetics, e.g. eye shadows and blush, are applied by people to improve their appearance. Skin care products are used to deal with imperfections of the skin or to protect it. Furthermore, skin lightening cosmetics are used for skin discoloration. In all cases, it is important to assess the quality and safety of cosmetic products, due to their widespread use all over the world. In particular, the UE Regulation (EC) No 1223/2009 prohibits the use of the so-called "heavy metals" as ingredients; however, their presence is allowed at technically unavoidable trace levels, provided the products are safe.

The knowledge of the total concentrations does not provide enough information on metal effect and behaviour in humans. In this work we studied the permeability of metals through the skin by *in-vitro* tests with Franz diffusion cells fitted with pig skin as a model membrane, to simulate human skin. We studied some decorative cosmetics and some skin lightening creams. Attention was focused on chromium and mercury, for their high potential toxicity. The pseudo-total concentrations of these metals and of other common elements (Al, As, Cd, Co, Ni, Pb) was determined by ICP optical emission spectroscopy after mineralization of the samples in a microwave oven. Mercury was introduced into the spectrometer in the form of cold vapour, to increase selectivity and sensitivity.

In the subsequent step of the study we performed permeation tests with Franz cells. The sample under investigation, defined as "donor phase", was applied on the model skin and after incubation at 32 ± 0,5 °C for 24 hours, three metal fractions were distinguished: the receiving solution; the amount retained inside the skin; the amount remaining in the donor phase. Preliminary experiments were carried out with synthetic standard solutions as donor phases, to verify the completeness of recovery. Then the permeation of metals from commercial products was tested. Chromium was mainly left in the donor phase, whereas meaningful amounts of mercury were found in all fractions. In the next steps of the study, experiments with other elements and other product, purchased from different commercial channels, will be carried out.

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Poster

Ambienti e Beni Culturali

ABC-P1

ANALYTICAL-PETROGRAPHIC STUDY OF BUGNATO DEGRADATION OF AN ANCIENT MILAN BUILDING

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The use of Rustic Ashlar (Bugnato) dates back to the end of the Roman Republican period when large building stones not only served as load-bearing function but also became an architectural element. The Bossage made with real natural stones ended in the early 1990s, replaced by concrete cast in formwork [1]. We were asked to characterize a bugnato fragment, coming from the facade of building Giachi-Amman, dated 1883, located in Via S. Raffaele in Milan (Italy), which shows clear signs of advanced deterioration (fig.1). Preliminary analyses evidences a high content of sulphate that, as it is well known, is the most dangerous salt for stones due to the high number of water coordination molecules that implies a high increase in volume of the crystals with the relative high pressure on the pore net of the stone. Acetic acid attack evidenced the carbonatic nature of the stone with about 61% of carbonate that obviously makes the stone high sensitive to acidic environments. This was confirmed by minero-petrographic analysis that revealed that the investigated sample is a matrix supported conglomerate made up of rounded to sub-angular clasts (max grain-size 12 mm), abundand sandy fraction, micrite and carbonate cement. Clasts are polygenic metamorphic igneous, sedimentary (quartz, muscovite, feldpsars) and the rock porosity is low (2-3 %). The observed microstructural and petrographic features are consistent with the Pleistocene sedimentary formations, made of fluvial and glacial deposits, widely found in the Adda and Brembo valleys, known as the mezzano variety of the *Ceppo del Brembo*. The Ionic Chromatography analyses (Anionic and Cation) on some incoherent samples were performed according to UNI-EN 16455:2014; the pH, μS, ORP and absorption spectrum in UV-Vis were also measured on the solution coming from the sample preparation. Such preliminary data already allow us to assert that the copious carbonate fine matrix and cement makes the lithotype easy weatherable, especially in an urban environment, and the main deterioration pattern is the sulphatation.

Fig. 1: The Bossage under study with evident damage due to flaking and exfoliationt. Samples are taken from areas already decoached without further damage to the artwork

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ABC-P2

LEACHATE FROM LANDFILL OF MUNICIPAL SOLID WASTE: CHARACTERIZATION AND DETERMINATION OF THERMODYNAMIC PROPERTIES

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Landfill leachate is an aqueous matrix generated by the percolation of rainwater into the body of a landfill and must be considered as a waste due to its content of natural and xenobiotic organic matter and heavy metals. Dissolved organic matter (DOM), which originate from a series of biological and chemical processes, is an important component of leachate because can act against dissolved metals through complexation reactions[1]. The thermodynamic properties of the leachates are bound to the acid-base properties of the DOM and to the sequestering ability towards metals. The purpose of my research is to study the leachate of municipal solid waste landfills by the characterization of their chemical-physical and thermodynamic properties and evaluate their possible use, in the perspective of the circular economy, as a metal sequestering agent. For this purposed, 5 leachates/waters contaminated by leachate were collected, according to the guidelines of Legislative Decree 152/2006, from a landfill of municipal solid waste in two different periods of the year (November and June). In a first time, analyses were carried out for the determination of the chemical-physical parameters according to Table 2 groundwater of the of Legislative Decree 152/2006[2]. The acid-base properties of the leachate were determined by potentiometric titrations in absence of ionic medium and in NaCl($_{aq}$), at I = 0.15 mol dm^{-3}, and T = 298.15K, processing the experimental data with the use of the Poliprotic Like model[3], already tested on many classes of high molecular weight polyelectrolytes. Information on the main composition of the leachates were obtained by means of ATR-IR and SEM EDX investigations on the dry residues obtained at T = 383.15K and at 923.15K after calcination. The complexes formation of leachates towards Cd^{2+}, Zn^{2+} and Cu^{2+} has been studied in $NaCl_{(aq)}$ at I = 0.15 mol dm^{-3} and T = 298.15K, by using the ISE-[H^+] potentiometry and voltammetry. The sequestering ability of leachates towards the metals ions was quantified at different pH values by means of the $pL_{0.5}$ parameter[4], proving that each leachate behave differently and still possesses the ability to complex metals.

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ABC-P3

PYRENE REMOVAL FROM WATER BY NEW ADVANCED UP AND DOWN PHOTOCATALYST

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Polycyclic Aromatic Hydrocarbons (PAH) may pose a risk to human health, as these compounds are considered to be highly toxic, carcinogenic and/or mutagenic and bioaccumulative. As components of synthetic dyes, polycyclic aromatic hydrocarbons (PAHs) are present as contaminants in textile wastewater and, may pose a threat to environment.

In the context of water remediation, hybrid biopolymer represent a green materials able to reduce pollutants from environmental matrices. Unfortunately, these types of material show several limitation concerning their use in large scale.

The aim of this study is to propose a new advanced up and down materials able to adsorption contaminants from water and carry it on surface in order to promote photooxidation processes.

Pyrene was selected as model pollutant for Polycyclic Aromatic Hydrocarbons (PAHs) and modified Hematite Montmorillonite Alginate Calcium Carbonate beads (@HeMaCaBeads) were prepared and characterized.

Pyrene removal using several hybrid materials were studied by spectrofluorimetric investigation.

About 50 % of Pyrene was removed from water solution without stirring after two hours of water treatment.

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Acknowledgements:

Funding for this work was provide by Starting Grant of University of Catania for the project Advanced up and down photocataLYst for ChEmical applications (ALYCE)

ASSESSING SOURCES AND FRACTIONS OF METALS ASSOCIATED WITH BEACHED PLASTIC LITTER: A CASE STUDY IN LAKE COMO (ITALY)

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The understanding of metal labile fractions on plastic surface is paramount to completely assess the environmental risks of plastic pollution. Plastic objects include in fact a (variable) amount of metal-containing additives. In addition, plastic can adsorb metals on its surface in an environmental context[1]. The present work, therefore, aims at detecting the fractionation of metals in environmental plastic samples deposited along the shores of lake Como (Italy). Newly produced plastic items were also analyzed as control. Samples were characterized through infrared spectroscopy (IR) and scanning electron microscopy (SEM). Then, the total metal load was assessed by an acid digestion procedure. A direct extraction with ultrapure nitric acid (HNO_3) 2% *v/v* was secondly performed to detect labile metals[2]. Lastly, a three-step extraction scheme enabled the determination of physisorbed, carbonate-bonded and organic matter-bonded metals, respectively. After the digestion/extraction, 18 elements (Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Ag, Cd, Sn, Ba, Pb, U) were quantified through inductively coupled plasma mass spectrometry (ICP-MS) analysis. Results showed that environmental samples had a higher concentration of metals compared to virgin ones. Importantly, the former presented a high concentration of metals in the loosely bonded or acid extractable fractions, highlighting increased bioavailability. This work shed light on the changes in bioavailability of metals induced by plastic environmental ageing, and the adopted analytical approach helped to discriminate between the metals with a possible environmental origin and those derived from the leaching of polymer matrix.

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ABC-P5

ON THE BEHAVIOR OF DISPERSED MICROPLASTICS IN LEAD - CONTAMINATED WATERS

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The widespread diffusion of plastic waste in the aquatic environment and their effects have become among the main subjects of study of the worldwide scientific community[1,2]. Due to the degradation environmental phenomena of different type of plastic polymers their morphological characteristics are highly variable, as well as the size of their particles that can reach the micro and nanometre ranges (MPs, NPs).
What most worries the scientific community is that MPs and NPs have been found in the food chain of vertebrates and invertebrates and can accumulate in their tissues and organs[1,2]. Moreover, the dangerousness of NPs and MPs can be accentuated by their ability to adsorb organic and inorganic pollutants from the surrounding aquatic environment which can make them a vehicle of toxic substances in the organism of animals and humans[2,3]. With this in mind, here we report a study on the Pb^{2+} ions adsorption onto MPs. The adsorption capacities and affinity of polystyrene microbeads both functionalized with carboxyl groups (PS-COOH) and not functionalized (PS) towards Pb^{2+} ions were studied. Differential Pulse Anodic Stripping Voltammetry (DP-ASV) was used for the determination of metal ions in solution. Furthermore, the following instrumental techniques have been used to study the effects of Pb^{2+} ions adsorption on the morphological features and superficial charge of the MPs: Electrochemical Impedance Spectroscopy (EIS), Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX), ξ Potential, FT-IR. The preliminary results here reported, in accordance with literature findings, show a fairly good ability of MPs to adsorb toxic metal ions that increases the risk related to their bioaccumulation.

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Acknowledgements:
The authors acknowledge the support of the NBFC to the University of Palermo, funded by the Italian Ministry of University and Research, PNRR, Missione 4 Componente 2, “Dalla ricerca all’impresa”, Investimento 1.4, Project CN00000033.

ABC-P6

TRANSMISSION ELECTRON MICROSCOPY AND MICRO-RAMAN SPECTROSCOPY FOR THE CHARACTERIZATION OF NANOPARTICLES AS EMERGING CONTAMINANTS IN ANTARTIC SNOW SAMPLES

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The impact of anthropic activities in Antarctica is a debated issue. Research stations and facilities constitute local sources of contamination, however, beyond direct contamination episodes, the study of the long-range transport of emerging contaminants toward polar areas is an almost completely unexplored research field. Nanoparticles (NPs) are emerging contaminants prone to be atmospherically transported over long distances, therefore their analysis in polar environment is a challenging issue for assessing the impact on climate, pollution and weather[1]. In this study, snow samples collected by the National Antarctic Research Program (PNRA) in the coastal area of Victoria Land (Antarctica) during the 2020–2021 austral summer were analyzed by transmission electron microscopy (TEM) equipped with energy-dispersive X-ray spectroscopy (EDS) for the morphological and structural analysis of nanoparticles at the atomic-scale and the 2D chemical spatial mapping at the nanoscale. Micro-Raman spectroscopy was applied for the identification of the composition of the NPs in melted snow samples. The achieved results proved the presence of NPs with sizes ranging from a few nm to 150 nm. Among the mineral particles, aluminosilicates were the most representative, while phosphates and sulphates were found in lower amounts. Furthermore, nanometric and sub-micrometric particles of iron and titanium oxides, both in isolated and aggregated form, were detected in almost all the samples. Neither micro- nor nanoplastics were observed in the samples under investigation. Soot particles were also identified by TEM analysis and confirmed by micro-Raman spectroscopy: the presence of Raman peaks at 1345 cm^{-1} (the disordered, or d, peak) and 1575 cm^{-1} (the graphite, or g, peak) proved the presence of carbon blacks[2].

These findings will help to understand the environmental fate of emerging pollutants in the Antarctic ecosystem, being useful for improving the environmental management of these substances in the anthropized areas of origin.

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ABC-P7

NANOFUN-NANOCELLULOSE BASED MEMBRANES FOR WATER PURIFICATION

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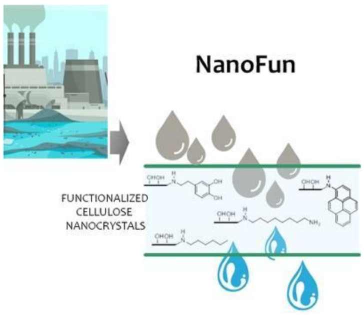
The problem of water purification requires urgent solutions to ensure the wellness of our society and a more sustainable preservation of the environment. Potential contaminants are heavy metals and highly concentrated salts, microbes, oils, persistent and emerging organic pollutants (POPs and ECs) and microplastics.[1]

Absorption technologies for the purification of polluted water are less expensive and more efficient and can be engineered relying on the use of sustainable biopolymer aggregates for the preparation of purification devices. Cellulose-based nanomaterials have demonstrated their very high potential in materials preparation[2,3] and have already been proposed as absorbers for water contaminants.[4] Nanocelluloses display high mechanical strength and specific surface area, are inexpensive and biodegradable and, more, they are amenable to surface chemical functionalization, which can enhance their absorption properties. Finally, cellulose nanofibers (CNFs) are considerably suitable for the preparation of stable filtration membranes.



The NanoFun bilateral project (2023-2025) on functionalized nanocellulose membranes between Italy and South Africa aims to design innovative and sustainable membranes for water purification, based on cellulose nanofibers (CNFs) and/or nanocrystals (CNCs), functionalized on the surface to modulate their ability to retain water contaminants: enrichment with negative surface charges or with lignin will be useful for retaining metal cations; functionalization with aromatic groups or lignin will serve to retain non-polar organic pollutants; ester groups (stearic transesterification with lipids) will be used to retain oils or emerging pollutants. The activities will include the preparation and functionalization of CNF and CNC, the preparation of the membranes, validation and the application to the purification of waters produced by companies or coming from polluted sites. Finally, a microfluidic filtration device will be assembled.

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ABC-P8

OPTIMIZATION OF A METHOD FOR THE ULTRATRACE LEVEL ANALYSIS OF POPs FROM POLAR AQUEOUS MATRICES

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The work is about the optimization of an analytical method for the determination of persistent organic pollutants at ultratrace levels in polar aqueous matrices (sea and lake water, ice core). One hundred and thirty compounds have been determined, belonging to four environment pollutants classes (chlorobenzenes, polychlorinated biphenyls, polychlorinated naphthalenes, polycyclic aromatic hydrocarbons). The analysis optimization was about the extraction and instrumental analysis.

The extraction part was carried out using MEPS technique for reducing the sampling volume and a safe and rugged procedure was optimized. In order to verify the method applicability, real Arctic and Antarctic samples have been analyzed.

The concentration levels of organic pollutants in polar samples are extremely low (in the order of ng/L[7–9]), it was necessary to develop an analysis method that was as effective as possible and at the same time capable to allow easier management of sampling operations, minimizing the sample volumes involved. A change from a volume in the order of tens of liters, necessary for the classics[1-2] liquid-liquid extractions, to just a few milliliters, can also make a significant contribution for future analysis of samples from polar ice cores. In fact, given that these are made up of the overlapping and subsequent compaction of the deposited snow layers, being able to conduct the analysis on a smaller sample volume,[3] and therefore on a smaller core thickness, it allows a higher temporal resolution, providing the possibility to analyze replicates of the same sample and to monitor more analytes in the same time period.

Instrumental analysis aimed at developing an MRM method and making the most of the available GC-MS/MS instrumentation. Therefore, a method for acquiring signals in MRM mode was developed. In particular, the instrument used is equipped with software that allows you to work in dynamic MRM mode (dMRM).

The classic MRM method need to divide the time in which the elution took place in some macro-windows, where the instrument is forced to monitor the transitions corresponding to the compounds that eluted within that specific time interval. With the dMRM mode, on the other hand, the retention times (RT) corresponding to the peaks of each compound are supplied to the instrument and the instrument is forced to monitor the corresponding transitions, for a small interval of time around each retention time. The advantage therefore lies in the fact that the dMRM mode allows you to monitor the transitions only for the time strictly necessary, minimizing the number of transitions monitored simultaneously and thus maximizing the dwell time.

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Acknowledgements: PNRA18_00194 and PRIN AMICO (2017)

ABC-P9

KINETICS AND TRANSFORMATION MECHANISM OF AN ANTIPSYCOTHIC DRUG TREATED WITH C_3N_4 BASED MATERIALS

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There is a growing public and scientific concern about the effects on ecosystem and human health posed by the presence of pharmaceuticals in the environment. Over the last few decades, the occurrence of pharmaceutical compounds, including psychiatric drugs, in the aquatic environment (i.e. drinking water, groundwater, surface water and treated water) was assessed. These compounds are likely to reach the aquatic environment mainly through effluents from wastewater treatment plants and hospitals, as a result of not being degraded or removed by conventional wastewater treatment plants and hospitals, and can be detected at very low concentrations level. The exploitation of Advanced Oxidation Processes is among the possible ways for increasing the treatment efficiency. In particular, the use of photocatalysis could be a powerful solution for environmental remediation.

New photocatalysts characterized by a g-C_3N_4-ZnO heterojunction were produced starting from different precursors, fully characterized and tested toward the abatement of clozapine, an antipsychotic drug. Experiments were conducted using a sun simulator and the evaluation of clozapine removal was assessed via HPLC-HRMS both in some actual water matrices and on the drug tablet in order to assess the role played by natural organic matter and by the excipients on the drug removal efficiency, respectively. In all cases, the tested materials allowed to easily achieve the complete abatement of the target molecule. Mechanistic studies evidenced that the drug transformation involved the formation of 19 transformation products identified and characterized via LC coupled with high resolution mass spectrometry (Orbitrap) with an electrospray ionization source in positive mode. The accurate mass of each degradation product was thus identified, so allowing to obtain the empirical formula for all by-products. MS^2 and MS^3 spectra analysis permits to assign a tentative structure for most of the transformation products.As for the reactive species, OH radicals are the key reactive species involved in the pollutant removal, while other species such as superoxide radical anion ($O_2•^-$) and especially singlet oxygen (O_2^1) played a marginal role in the degradation process.

Acknowledgements:
The authors acknowledge SusWater project funded within the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 101007578.

ABC-P10

INVESTIGATING ARSENIC ADSORPTION AND DESORPTION IN THE COMO AQUIFER (ITALY): IMPLICATIONS FOR CONTAMINANT SEQUESTRATION AND MOBILITY IN GROUNDWATER

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Understanding the interaction between sediment properties and metal ion characteristics and their impact on the distribution of heavy metals between solid and liquid phases is crucial for effectively controlling urban water systems. This research investigates the integrated influence of groundwater and sediment characteristics on weakly-bound inorganic arsenic behaviour in the context of adsorption and desorption processes. The specific emphasis of this study stems from the naturally occurring arsenic concentrations in the Como aquifer (Lombardy, Italy), which exceed regulatory limits[1]. The sampling protocol and the analytical techniques applied were designed to capture a representative range of spatial locations and vertical profiles within the aquifer system. Samples were obtained to facilitate comprehensive analysis and characterisation of As mobility, thereby enabling a detailed assessment of the hydrogeochemical dynamics and behaviour of the contaminant being sequestered from the surrounding water matrix. Firstly, sediment samples were characterized using energy-dispersive X-ray spectroscopy (SEM-EDX) to identify mineral phases and potential adsorption sites, while inductively coupled plasma-mass spectrometry (ICP-MS) was used to quantify As(III) and As(V) background concentrations in water samples. Experimental design (DOE) was employed to validate the essential conditions necessary for the successful execution of adsorption and desorption kinetic experiments. The optimized experimental parameters were established through systematic manipulation of critical factors, including contact time, initial concentration, and pH, ensuring robust and reliable assessments of the target analyte's dynamic adsorption and desorption behaviour. Preliminary results suggest that the sediment exhibits a considerable adsorption capacity for both As(III) and As(V) species, with a maximum adsorption capacity of As(V), indicating stronger sediment affinity toward arsenite. Experiments further demonstrated that arsenic exhibits high adsorption potential under specific conditions (i.e. acidic to neutral pH range). These findings shed light on the potential circumstances that could lead to arsenic mobilisation and subsequent transport within the groundwater system. By elucidating the processes governing arsenic interactions with sediment, this study provides valuable insights into the fate of arsenic in natural systems.

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ABC-P11

A SYMPOSIUM IN THE LAB: DISCOVERING WINE MOLECULAR MARKERS IN ANCIENT POTTERY THROUGH HPLC-MS/MS

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The analysis of organic residues in ancient remains and archaeological artifacts presents the great potential of returning new deepening information about ancient populations[1,2], from the manufacturing techniques to the agricultural evolution, to the trades and exchange contacts among civilities. In particular, the determination of wine markers represents a pushing challenge in archaeometry, with reference to the importance and the consumption of this beverage in ancient times[3]. In the frame of the project *Imag-ORA. Beyond Images in Context. A new interdisciplinary approach for the study of uses and functions of figured pottery in Preroman Italy* (P.I.: A. Pola), a research line has been devoted to support the work of archaeologists through the development of a new analytical methodology dealing with the main issues of Cultural Heritage diagnostics: limited amount of samples, need of micro-invasiveness, requirement of avoiding chemical artifacts. In this study, the design of a new analytical method, applicable to ancient vessels of pre-Roman age, is presented: the procedure involves a derivatisation and a clean-up step for the subsequent analysis by HPLC-MS/MS. Several factors for the development of the analytical approach were deepened, from the typology of the best clean up, the nature of dispersing and extracting phases, the interfering species from the matrix. The new analytical method has been dedicated to a series of vessels found in the Faliscan area. The preliminary data are very promising in order to show for the first time a comprehensive study of the use and function of valuable figurative pottery from this period.

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ABC-P12

CURSE OF THE ANCIENT DYES: A MULTI-ANALYTICAL STUDY OF TEXTILE FRAGMENTS FROM TUTANKHAMUN'S CHAMBER

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When the archaeologist Howard Carter discovered the Pharaoh Tutankhamun's chamber in 1922, after the study of the main objects he deposited the remaining materials of the tomb in a wooden box. Those started to be subjected to analyses in 2018 and great efforts were dedicated to the identification of dyes of some textile pieces dating back to 1325 BC, the year of Pharaoh's death. After preliminary analyses by means of non-invasive Visible light Fiber Optic Reflectance Spectroscopy[1], the gel-supported liquid extraction was applied for the on-site extraction of the dyes[2]. The substrates were initially analysed by means of Surface Enhanced Raman Scattering spectroscopy, and then processed by Dispersive Liquid Liquid Micro-Extraction, specific designed for natural dyes, and subjected to HPLC-MS/MS analysis. The dyes in the areas of the samples were identified, and information about their degradation products were achieved. The combination of non- and micro-invasive analytical techniques resulted highly proficient, while it was possible to evaluate the complementarity of the different methodologies in the information recovery from a historical case study.

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ABC-P13

THE UCUPE MASK'S MYSTERY UNVEILED: A COMPREHENSIVE CHARCTERISATION OF METALS AND ADHESIVES EMPLOYED IN ITS CREATION

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The aim of this study is to characterise the materials used for a funeral mask discovered in the tomb of the Lord of Ucupe in Lambayeque, Chiclayo, Peru. The mask belongs to the Moche culture, which flourished in northern Peru from 100 A.D. The mask is made of a metallic alloy, while the eye sockets contain a dark substance employed for stick the pupils [1]-[3].

Various analytical techniques, such as ATR-FTIR, Py-GC/MS, GC/MS, and SEM-EDS were employed to investigate the dark substance. The characterization of the material shows the presence of a resinous substance with small inclusions of gypsum and phyllosilicates. The main organic compounds identified were triterpenes, primarily characterized by a lupane structure, as well as flavonoids and lipids. These findings seem to suggest that the material is a pitch or tar originated from the bark of higher plants. However, the lack of an extensive database on South American plants hindered the precise identification of the genus.

For the characterization of the metal alloy technique, X-Ray fluorescence (ED-XRF) coupled with Monte Carlo simulation was utilized. The analysis revealed a silver-plated copper, a less commonly encountered technique compared to gold Tumbaga. In addition, the simulation showed a silver depletion on the surface due to the corrosion.

In conclusion, the comprehensive characterization of the mask using a multi-analytical approach was crucial in uncovering significant details. This study provides the first evidence of pitch or tar being used as an adhesive in an archaeological artifact from South America. These findings add valuable insights into the sourcing of materials and technologies employed by the Moche culture, thus expanding the existing knowledge on South American civilizations.

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ABC-P14

SILVER NANOPARTICLES FROM ORANGE PEEL EXTRACT AS SELECTIVE SENSOR FOR LEAD IONS IN AQUEOUS SOLUTIONS

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Orange peels represent one of the precious waste materials that is composed mainly of cellulose, pectin, hemicellulose, lignin, flavonoids, chlorophyll pigments and other low molecular weight hydrocarbons containing various functional groups, such as carboxyl and hydroxyl[1]. In addition, flavonoid compounds are interesting for their antioxidant properties that can be applied in the reduction of metal ions into nanoparticles[2].

Silver nanoparticles (AgNPs) can be used as a surface plasmon resonance (SPR) colorimetric sensor; the correlation between the SPR phenomenon and the aggregation state of nanoparticle allows the real-time detection of a target molecule. Surface functionalization of NPs with proper molecular baits is often performed to establish the selectivity of the sensor[3].

Orange Peel Water Extract (OPE) was prepared by adding ultrapure water to orange peel and stirring at 40°C, filtering, and cooling. The freshly obtained OPE was used immediately after filtration or frozen until use.

This study exploits the synthesis of green silver nanoparticles (AgNPs) by using orange peel extract as reducing and functionalizing agents. The AgNPs were characterised by scanning electron microscopy (SEM), energy dispersive X-ray analyzers (EDX), DLS and infrared spectroscopy.

These nanoparticles have been demonstrated to be spherical, with a maximum diameter size around 25 nm, and were shown to associate into larger clusters in the presence of divalent cations dependind on type and concentration.

Specifically, these AgNPs were successfully used as selective sensor to detect micromolar levels of Pb^{2+} at concentration below 6.6×10^{-5} M. In this concentration range, the aggregation process led to a major change in optical properties of the AgNPs suspension, consisting of a red shift of the SPR band at 405 nm with a progressive linear decrease in the intensity as function of the concentration.

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ABC-P15

BERGAMOT POMACE ADSORBENT MATERIAL FOR THE REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS

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In the last years, citrus processing waste has been used as a second raw material for multifunctional materials development capable of effectively and selectively interacting with organic pollutants, such as pesticides (POPs) as well as inorganic pollutants like metals and anions [1], through adsorption mechanisms. This contribution presents the preliminary results of an investigation focused on the potential of materials derived from bergamot citrus industry waste to be used as sequestrant agents [2] for metal ions in multicomponent solutions that simulate natural fluids conditions. After confirming the presence of functional groups capable to interact with metal ions through FT-IR ATR spectroscopy, potentiometric measurements were carried out at t = 25 °C and in an ionic strength range between 0.1-1 mol L^{-1} in $NaNO_{3(aq)}$. This technique allowed for the evaluation of pomace acid-base properties and the experimental data were analyzed using the *Focus* model [3]. To assess the adsorption selectivity of the material obtained, batch experiments were performed on a multicomponent solution containing Pb (II), Cd (II), Cu (II), Zn (II), and Ni (II) ions [4]. The concentration of each ion was determined by ICP-MS. Moreover, release experiments were carried out to assess the potential reuse of the material. Various desorbent agents (HCl, HNO_3, GLDA, EDDS) were used to extract the metal cations [5]. Such as use of citrus processing waste as a second raw material offers a sustainable and environmentally friendly approach to address pollution challenges by transforming waste into functional materials for pollutant remediation.

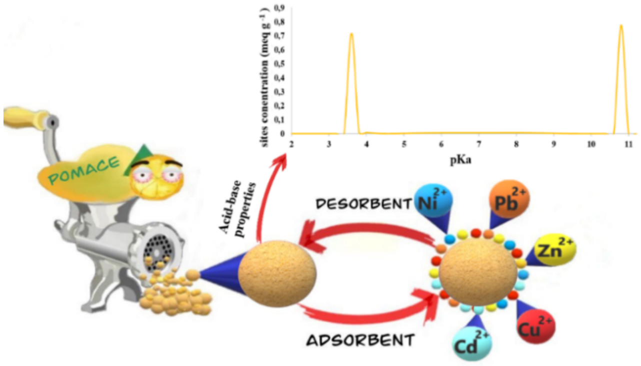

Figure 1: schematic representation of the studies performed on bergamot pomace

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ABC-P16

ASSESSMENT OF BIODEGRADABLE PLASTIC FATE IN THE ENVIRONMENT: INVESTIGATING BIODEGRADABLE MULCH FILMS

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In the last few years, biobased and biodegradable polymers have been considered a potential solution to the emergency of plastic pollution in the environment. Agricultural mulch films provide multiple benefits for crop production, and the problem of their recovery and disposal can be addressed by using biodegradable plastics. Biodegradation can be defined as a system property, that depends on the specific material, and on the conditions of the environment receiving it. The complexity of biodegradation calls for the development and application of analytical methods to investigate and characterise biodegradable polymers and their lifecycle, and to assess their degradation pathways.

Thermoanalytical methods are emerging for characterizing plastic debris and microplastics in the environment, however their application to biodegradable products is still limited. We investigated the potential of analytical pyrolysis coupled to mass spectrometry in the life cycle assessment of agricultural mulch films.

Biodegradable mulch films made of poly(lactic acid)(PLA)/ poly(butylene adipate-co-terephthalate)(PBAT) and Mater-bi (Starch/PLA/PBAT) were exposed to the open environment (air, soil, marine water), and samples were collected after 1, 3, 6 and 12 months. The materials were investigated by scanning electron microscopy (SEM) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). The formation of holes and visible damages on the surface of all degraded subsamples was observed, both in soil and in air. Py-GC/MS highlighted the disappearance of additives, suggesting a possible leaching in the environment. Both in soil and in air, signs of PBAT degradation were detected from 6 months, and oxidation products at 12 months.

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ABC-P17

ANALYTICAL PYROLYSIS FOR THE CHARACTERIZATION OF PAINT MATERIALS IN STREET ART IN THE PRIN PROJECT "SUPERSTAR - SUSTAINABLE PRESERVATION STRATEGIES FOR STREET ART"

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In the last decade, works of street art, located outdoors in urban contexts, have received increasing attention from cirizens, institutions, art historians and conservators, due to their acknowledged social and cultural relevance [1].The ephemeral character, free access, and exposure to the environment and anthropic actions, make indeed public paintings vulnerable to neglect, removal, vandalism, and degradation. Beyond that, the strategies aimed at their preservation and fruition are rather unclear or lacking. The Italian project Prin2020 "*Superstar-Sustainable Preservation Strategies for Street Art*" sets as a goal the definition of innovative guidelines for a sustainable preservation strategy of street art, aimed at safeguarding its powerful social and cultural message in the urban context (https://prin2020superstar.dcci.unipi.it). The availability of effective analytical tools for the identification of artwork materials is thus crucial to support defining the best preservation practices. The cooperative consortium for the project is composed of University of Pisa (project coordinator Prof. Francesca Modugno); University of Bologna (Prof. Silvia Prati), Politecnico di Milano (Prof. Lucia Toniolo), University of Turin (Prof. Dominique Scalarone) and CNR -Perugia (Dr. Laura Cartechini).

Superstar project case studies include two prominent public mural paintings located in Milan, selected with the support of Comune di Milano (Area Museo delle Culture, Progetti Interculturali e Arte nello Spazio Pubblico, Dr. Marina Pugliese and Dr. Alice Cosmai): Or.Me by Orticanoodles in Via S. Faustino (2017) and Necesse by SMOE in via Ludovico di Breme (2021). The two murals have been the object of study of an extensive in-situ non-invasive campaign of measurements carried out by CNR-Perugia [3]. Within this analysis campaign, it was possible to collect some samples from damaged and altered areas in the mural paintings.

The poster describes the results obtained in the analysis of the paint samples by analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS), applied to characterise paint binders and organic additives in the paint formulations [4]. The analyses allowed for the identification of paint binders in the two murals and were interpreted contextually with the results of non-invasive external reflectance Fourier transform infrared spectroscopy (FT-IR). In particular, polyvinyl acetate plasticised with Veova and styrene-acrylic resins were detected in Or.Me, while a nBA/MMA acrylic resin was the binder in Necesse.

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ABC-P18

Cr(VI) ABSORPTION BY SILICA TRANSPARENT XEROGEL MONOLITH: SPECTRAL AND KINETIC STUDY

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Chromium is used in different industrial processes such as leather tanning, electroplating, textile dyeing and plastic productions, with the generations of hazardous waste containing relatively high amounts of chromium. In the environment, chromium exists as Cr(III) and Cr(VI) with the hexavalent chromium 100 times more toxic than the trivalent form; exposition to Cr(VI) can causes allergic reactions, asthma eyes irritation, lung and kidney cancer[1]. Cr(VI) is highly soluble and mobile in water solution and can be present in different species, depending on its concentration and the pH of the aqueous environment[2].

In this context, a transparent silica-based xerogel has been optimized by using sol-gel technique at low temperature (50°C). The disk-shaped xerogel was characterized by Raman, Scanning Electron Microscopy (SEM) and BET measurements. The material showed silica amorphous phase and high porosity and prominent absorption results towards different concentrations of Cr(VI) as $HCrO_4^-$. In addition, the absorption kinetics of Cr(VI) were evaluated by studying different models, showing that the absorption took place by intra-particle diffusion process and the absorption equilibrium followed a Freundlich isotherm model. The xerogel can be reused after the reduction of Cr(VI) to Cr(III), by the treatment with 1,5-diphenylcarbazide[3].

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ABC-P19

QUANTIFICATION OF MICROPLASTICS AND POLYMER ADDITIVES IN AIRBORNE PARTICULATE AND SETTLED DUSTS COLLECTED IN INDOOR ENVIRONMENTS

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The widespread use of synthetic polymers has led to a significant environmental crisis caused by plastic pollution, with microplastics being found in various environments and posing risks to both human health and the ecosystems. The potential for plastic fragments to disperse in the air as particulate and to be inhaled by humans, potentially causes harm to the respiratory and other systems. Therefore, there is a particular need to study microplastics as air pollutants. In this study, we tested a combination of analytical pyrolysis, gas chromatography, and mass spectrometry, as well as gas and liquid chromatography-mass spectrometry, to identify and quantify both microplastics and their additives in airborne particulate matter and settled dust from two work environments. By using this combined approach, we were able to accurately quantify ten distinct synthetic polymers as well as eight classes of polymer additives. The determined additives include phthalate esters, adipates, citrates, sebacates, trimellitates, benzoates, organophosphates, and newly developed brominated flame retardants.

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ADVANCEMENTS IN SAMPLING STRATEGIES FOR ASSESSING POPs: PRE-LABELED ACTIVE CARBON FIBERS VS QFF/PUF

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Due to the potential hazardous effects of POPs such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins/polychlorinated dibenzo-furans (PCDD/Fs) on people and wildlife [1,2], their monitoring in the atmosphere is important. They exist in the atmosphere as semi-volatile organic compounds (SVOCs) in both the gaseous and particulate phases, and several standard reference methods require a quartz fiber filter (QFF) to collect particle-bound contaminants, followed by a cartridge filled with a solid sorbent, (i.e. polyurethane foam (PUF) or styrene-divinylbenzene polymer (XAD-2 resin)), to collect the compounds in the gaseous-phase. Using the isotopic dilution approach, standard solutions containing ^{13}C-labeled compounds are added in three separate phases of the analysis. To validate the sampling process, a sampling standard solution (SS) must be spiked on the filter, prior to sampling, directly on the sampling site and the recovery rate of each congener must fall within a given range. On site spiking has both pros and cons: it reduces the possibility of the standard being lost due to degradation or volatilization while being transported, but it is a time-consuming and hazardous operation (carcinogenic labeled substances). That said, practical, long-lasting, and ready-to-use pre-labeled filter would be ideal. Recently, Cerasa et al. (2023) assessed efficient sampling and extraction of SVOCs from active carbon fiber-based (ACF) sorbents in air sampling [3]. In this paper, the most common critical issues related to the SS spiking step will be discussed, as well as the effect of temperature storage and the stability of the sampling standards added on ACF over three months. The aim of this research is to show that a pre-labeled ACF can advantageously replace QFF/PUF and eliminate the need to spike it on the field.

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QUANTITATIVE DETERMINATION OF TRACE OR ULTRA-TRACE LEVELS IN COMPLEX NATURAL SYSTEMS: A STRATEGIC STRATEGY FOR RARE EARTH ELEMENTS

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The crucial challenge in analytical determinations of natural systems is establishing data quality and generating reproducible values. Validation protocols require the use of reference materials and/or reference data and multiple initial trials are needed as error decreases with the number of replicates. When it's not possible to compare one's system with a validated one, which is common when studying natural systems, difficulties are intensified especially when dealing with analytes in trace concentrations, limited sample volumes, a small number of samples and complex matrix.

In this work, we have assessed the variability in quantitative determinations of ultra-trace levels of Rare Earth Elements (REE) in a small volume of solution (less than 250 µL, resulting from sampling the xylem-sap of *Vitis vinifera L*. Here, the concentrations of REE is close to the quantification limit. In addition, official data and certified materials for REE in xylem-sap are not available. Our protocol is based on comparing the variance of real xylem-sap sample with an in-house reference material (water spiked with REE) at critical values (near the limit of quantification), as well as at different concentrations of REE. The results of our strategic validation allow for proposing a chart of critical parameters to be considered when developing data quality ensuring that the analytical determinations remain under statistical control throughout the year-long experimental period.

Acknowledgement:
This work is part of the doctoral thesis of the first author supported by Università degli Studi di Palermo and the Sorbonne Université Paris.

ABC-P22

CHARACTERIZATION OF *HELIX ASPERSA ASPERSA* FLAVOUR: NUTRITIONAL AND POLLUTION EVALUATION

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Helix aspersa is a phytophagous pulmonated gastropod mollusk, which is also detritivorous and occupies various levels in food chains[1]. In certain countries, humans consume *H. aspersa* as part of their diet. Additionally, *H. aspersa* is commonly bred for gastronomic or cosmetic purposes, specifically for slime production. However, the current methods of stimulating slime production often involve less invasive manual systems or more efficient equipment that, however, could lead to the death of the gastropods. Considering the potential future utilization of waste products from the supply chain, which may include gastropods unsuitable for the cosmetic or food industry, this study aimed to evaluate the nutritional properties of flours (fatty acids profile, fat matter, proteins, aminoacidic profile) obtained from snails bred in Italy on an organic farm for slime production purposes. Furthermore, laboratory-produced flour samples were analyzed to ensure the absence of organic pollutants, such as PAH, PCB, and PBDE since these mollusks are capable of accumulating contaminants present in the soil and air[1,2,3].

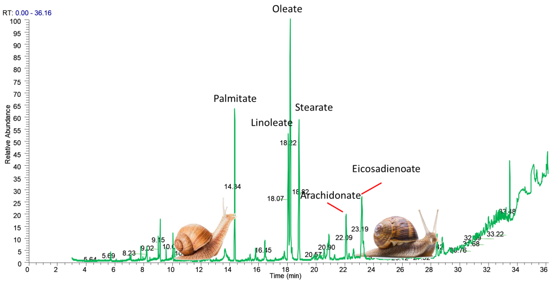

Figure 1: GC/MS chromatogram of *Helix aspersa* flour FAMEs.

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ABC-P23

ANALITYCAL METHOD FOR BISPHENOL A (BPA) CONJUGATED/FREE DETERMINATION IN BIOLOGICAL FLUIDS SAMPLES

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The method here described is developed for the analysis of bisphenol A (BPA), a compound with endocrine disrupting action, critical for human and environmental health[1,2], in samples of biological fluids (serum, but the method is also appropriate for milk). The method leads to the determination of the free/conjugated fraction of BPA and, for this reason, two complete analyses are carried out in parallel on the same sample. Enzyme glucuronidase was added to a first aliquot of 0.5 ml of serum sample and were placed in an incubator at 37 °C for 12 hours. The incubation of the sample with the glucuronidase enzyme allows the evaluation of the total concentration of the contaminant, including free BPA and conjugated BPA, i.e. already metabolised. A second aliquot of sample undergoes only the procedure described below, without the preliminary step of deconjugation, therefore the result represents only free BPA. Ethyl ether was added to both sample aliquots, shaken and subsequently centrifuged. Thus constituted a subnatant and a supernatant, the latter was collected in a new test tube in "BPA-free" polyester. This procedure was repeated three times, and once the collection volume was reconstituted, the latter was evaporated under nitrogen flow and reconstituted in acetonitrile. Finally, it was filtered with a solvent-resistant nylon filter and brought to a final volume of 0.5 ml with acetonitrile in autosampler vials. For the analytical determination of BPA, each aliquot was injected into a LC-ESI-MS system, which uses a Betasil C18 50x2.1 mm column at a flow rate of 250 µL/min. The mobile phases used were acetonitrile and ammonium acetate, according to a defined solvent program. The ESI-MS system operates in negative mode. The negative ion useful for the identification of BPA was obtained by fragmentation of the 227 ion with a collision energy of 35 eV and production of the ion (m/z) 212. Several tests were carried out to calculate the recovery percentage of the process, that resulted between 85 and 90%. The limit of detection (LOD), defined as 3 times the signal-to-noise ratio, were equal to 0.5 ng/ml for BPA. The results obtained for each sample, by subtracting the unconjugated BPA value (aliquot without enzyme addition) from the total BPA value (aliquot with enzyme addition), give a crucial indication for the interpretation of the exposure data in biological samples. For this reason, this method can be usefully employed in analyses in biomonitoring and in studies of exposure to this environmental contaminant of priority interest[3].

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ABC-P24

TEACHING AND TRAINING ACTIVITIES IN THE FIELD OF HERITAGE SCIENCE: THE ROLE OF ANALYTICAL SPECTROSCOPY AND CHEMOMETRICS

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Heritage science encompasses various disciplines from the humanities, sciences, and engineering, aiming to deepen the understanding, preservation, and sustainable use of cultural heritage, thereby enriching cultural and economic potentialities of countries and individuals. To this purpose, it is quite challenging to adapt any training and education activity to the multi-disciplinary audience of actors involved in heritage science.

Therefore, one of the main objectives of the European project IPERION HS project (G.A. n. 871034) is to establish appropriate educational guidelines and provide targeted training activities for professionals in the field of heritage science.

Specifically, the development and utilization of spectroscopic techniques in combination with chemometric methods have demonstrated a pivotal role in studying complex and heterogenous systems, enhancing the useful information embedded in data.

While there has been a recent surge in recognizing the potential of chemometric approaches, it is now more crucial than ever to address the proper training of scientists and operators. This is essential for cultivating a new scientific community capable of effectively applying chemometric tools and comprehensively interpreting outcomes to address conservation issues. In light of this recognition, a specialized lecture was included in the program of the first IPERION HS Doctoral Summer School (13th -16th July 2021, online organized by the University of Bologna). This lecture focused on the use of advanced spectroscopic methods and chemometric approaches for studying paintings, with particular emphasis on the advancement of suitable and progressively automated tools accessible to the entire community.

ABC-P25

SOLUZIONE MEDUSA-GC/MS, LA PIÙ RECENTE CRIOTECNOLOGIA APPLICATA ALL'ANALISI IN CONTINUO DI SOSTANZE CLIMA-ALTERANTI IN CAMPIONI DI ARIA

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L'Osservatorio Climatico Italiano "Ottavio Vittori" al Monte Cimone effettua misurazioni di routine automatizzate dei principali HFC, HCFC e altri alocarburi chiave, inclusi i composti perfluorocarburi più volatili, con la collaborazione dell'Università di Urbino.

Il monitoraggio completamente automatizzato è iniziato nel 2003, utilizzando la soluzione strumentale SRA basata su TD-GC/MS Markes-Agilent

Per superare le limitazioni pratiche legate alla volatilità dei composti perfluorocarburi più leggeri, è stato implementato il sistema Medusa-GC/MS.

Tra le soluzioni tecniche del sistema MEDUSA si annoverano l'estremità fredda Polycold "Cryotiger"e l'utilizzo di trappole doppie, che rendono possibile:

- l'analisi di una vasta gamma di composti grazie al raggiungimento di temperature estremamente basse, evitano inoltre potenziali reazioni tra analiti e trappole
- l'utilizzo di materiali adsorbenti appropriati,
- l'applicazione di ampi intervalli di temperatura programmabili
- la purificazione degli analiti mediante distillazione frazionata e rifocalizzazione.

Il sistema Medusa-GC/MS analizza campioni d'aria con una frequenza di 60 minuti, utilizzando un volume di 2 litri di aria campione per misurazione.

L'implementazione di questa strumentazione avanzata fornisce importanti informazioni sulla concentrazione atmosferica di questi composti nel bacino dell'Europa meridionale e del Mediterraneo settentrionale, contribuendo alla comprensione e alla gestione del cambiamento climatico. Le misurazioni a lungo termine fornite da questo sistema contribuiscono anche alla quantificazione dell'andamento delle sostanze clima-alteranti e degli inquinanti atmosferici.

ABC-P26

ON THE FATE OF HERBICIDES: SURFACTANTS/BIOSUBSTRATES AFFINITY AND TRANSPORT TESTS

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Among POPs (persistent organic pollutants), herbicides and pesticides may remain in the place of application for a long time.[1] Therefore, coming into contact with these compounds is very simple and understanding what types of interactions occur with different substrates is crucial for defining risk factors. Despite the many literature studies, the topic is investigated essentially from a biological point of view.[2]

In this frame, we found it interesting to perform some spectrophotometric and spectrofluorometric tests to contribute to quantifying the bio-membrane interaction, transport by proteins and bioaccumulation of some target herbicides (Figure 1). The systems used in this work vary in complexity, from simple micellar surfactants aggregates of different charge (sodium dodecyl sulphate-SDS, dodecyl trimethyl ammonium chloride-DTAC, Triton X-100), to choline liposomes (1-palmitoyl-2-oleoyl phosphatidylcholine-POPC), model proteins such as serum albumin, up to more complex systems such as marine sponges.

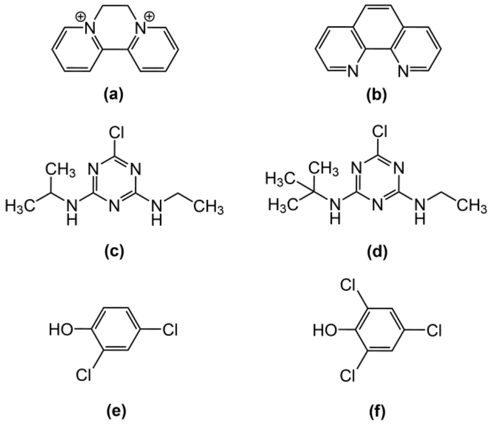

Figure 1: Herbicides (or herbicide components) analysed in this work: (a) diquat dibromide; (b) 1,10-phenanthroline; (c) atrazine; (d) terbuthylazine; (e) 2,4-dichlorophenol; (f) 2,4,6-trichlorophenol.

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Acknowledgements:
National research projects in Antarctica (PNRA) projects PNRA18_00194, PNRA18_00216 are gratefully acknowledged.

ORANGE PEEL WASTE AS SUSTAINABLE MATERIALS FOR POLLUTANTS REMOVAL FROM AQUEOUS SOLUTIONS

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World production of oranges is estimated at 75 million tons per year, and it is approximated that about 15 million tons of orange peel waste (OP) were generated in the world increasing every year[1].

Heavy metal ions are among the most released contaminants, and for this reason they are of particular concern[2]. Organic dyes, in addition, are coloured substances that tend to be very stable and hardly biodegradable, contributing significantly to water pollution[3]. The widespread presence of heavy metals and synthetic dyes in water bodies, their bioaccumulation, potential toxicity and negative health effects have made the study of their environmental fate very important.

The chemical compounds composing orange peel (OP) waste contain different functional groups, such as carboxyl and hydroxyl, making OP a potential adsorbent material for the removal of heavy metals and dyes from aqueous solutions[4].

In this study, *Citrus sinensis* peel wastes were valorised, to obtain materials usable for the adsorption of heavy metal ions and organic dyes, showing promising results.

For this purpose, OPs were cut up into small pieces, washed with water and dried in the oven at 40°C. OPs were successively saponified with NaOH to cleave ester bonds on the surface of peels to generate more hydroxyl groups, followed by thorough washing with deionized water to remove excess base. Washed peels were sonicated in 2-propanol to extract soluble organic compounds and then filtered, washed with water, dried, and chemically/morphologically characterized. This contribution reports preliminary results on the application of the OP as new absorbent materials in water samples containing a mix of heavy metal ions showing a selective sequestration of lead ions; OP materials were also applied for the absorption of several cationic dyes. The equilibrium and kinetic properties were explored for the absorption of both types of pollutants. Owing to the multifunctional characteristics of biopeels, adsorption of these pollutants is facilitated by a combination of processes, involving ion exchange, complexation, and electrostatic interaction[5].

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ABC-P28

PRELIMINARY TESTS TO EVALUATE THE PERFORMANCE OF A BOTANICAL BIOFILTER IN REMOVING INDOOR AIR POLLUTANTS

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Ensuring good indoor air quality (IAQ) is of the utmost importance given that people spend most of their time (about 80%) in indoor spaces1. In this study, an active botanical biofilter for indoor applications was tested in combination with two different types of plants (Chlorophytum comosum and Epipremnum aureum) for the removal of particulate matter (PM) and volatile organic compounds (VOCs). Preliminary analyses were conducted on a single module inside a chamber especially designed for experimental testing (Fig. 1). Lavander oil and denatured alcohol were chosen as the sources of VOCs, whereas paper was selected as the source of PM. Known quantities of air pollutants were generated with a burner operating at high temperatures, and the concentrations trends were monitored using appropriate sensors: an optical particle counter (P-Dust Monit, conTec Engineering s.r.l.) for PM, and a total VOC analyzer (NETPID, Lab Service Analytica s.r.l.) for VOCs. Removal and filtration efficiencies was calculated from the decay curves of each experimental test. Preliminary investigations showed promising results in the removal of both PM and VOCs, with filtration efficiencies greater than 90%.

Figure 1:Top view of the chamber with the biofilter module, the heater and the NETPID sensor.

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ABC-P29

EVALUATION OF THE METAL CONTENT IN TRUFFLE AND SOIL SAMPLES BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY AND CHEMOMETRIC DATA ANALYSIS

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The multielemental analysis of biological samples reveals potential correlations in the absorption of different metals, a phenomenon widely supported by scientific literature, especially concerning edible plant and fungal species. Among these, fungi stand out for their significant capacity to bioaccumulate heavy metals and toxic substances, making the assessment of their concentration concerning the surrounding soil crucial[1]. Truffles are edible fungal species of great economic value and may, in some cases, contain significant levels of heavy metals harmful to human health. However, the mechanisms governing metal absorption by truffle mycelium are still not fully understood, as they depend not only on soil characteristics but also on truffle species, bacterial colonies within the gleba, and involved host plants[2]. In this study, an analysis of metal content in truffle and soil samples was conducted from two different regions in Italy. The use of inductively coupled plasma mass spectrometry (ICP-MS) allowed the quantification of elements, even at ultra-trace levels. The collected data were subjected to chemometric analysis to identify possible correlations between the samples and comprehend the relationship between metal content in truffles and the composition of the surrounding soil (figure 1).

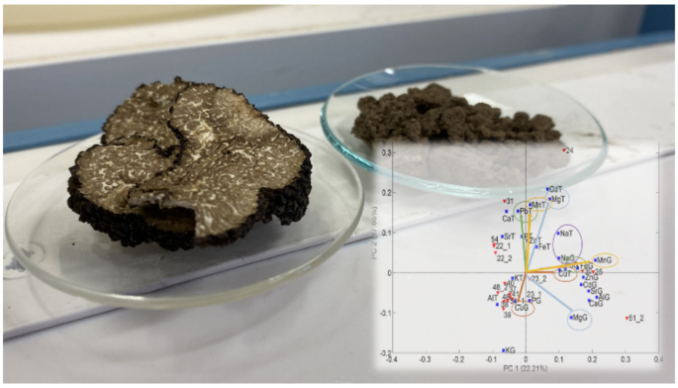

Figure 1: Dried truffle and soil samples.

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Poster

Green Chemistry

DIMETHYL CARBONATE AS AN ENVIRONMETALLY FRIENDLY ALTERNATIVE TO ACETONITRILE AS ORGANIC MODIFIER IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

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Reversed Phase Liquid Chromatography (RPLC) is the preferred method of separation for biomolecules such as nucleic acids, peptides, and proteins in the biopharmaceutical field. RPLC is favored due to its ability to separate, purify, and analyze these biomolecules with high resolution and large loading capacity, making it ideal for high sample throughput. The most commonly used organic modifier in RPLC is acetonitrile (ACN), which is popular due to its excellent miscibility with water and other organic solvents, its low viscosity, which results in low backpressure and high elution strength, and its ability to elute a wide range of compounds. Additionally, ACN is chemically stable, low reactive, and highly compatible with sensitive compounds. However, ACN has its drawbacks, such as its higher cost compared to other organic solvents like ethanol or methanol, and its toxicity, which can be hazardous since it can be converted to cyanide in the body[1]. The decision to search for greener alternatives to acetonitrile in RPLC was primarily driven by the need to reduce the environmental impact of biopharmaceutical production. Additionally, promoting sustainable industrial practices and ensuring operator safety were also key motivators. Therefore, researchers are currently working to develop new "green" organic solvents that are equally as effective and safe as acetonitrile, but with a reduced environmental footprint[2]. Recently, researchers have been exploring solvents beyond the well-known physicochemical properties of alcohols. One such solvent is dimethyl carbonate (DMC), which has been classified as one of the "green chemicals" by the U.S. Environmental Protection Agency (EPA) due to its high biodegradability and low toxicity[1]. DMC is currently used as a solvent in the energy storage industry (such as in the production of lithium batteries), as well as for the synthesis of polymers, paints, and coatings. Additionally, it is an excellent extraction agent in the biological field for separating organic compounds from complex matrices and is used for environmental applications as a solvent for contaminant analysis. Furthermore, DMC has been recently introduced as an organic modifier for chromatographic separations, with a pioneering study showing its use in high-performance liquid chromatography hyphenated to inductively coupled plasma mass spectrometry[3]. This study aims to investigate the possible use of DMC as a new organic modifier in RPLC from a fundamental perspective through a series of case studies, by considering not only small molecules but also larger biomolecules (e.g., peptides).

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GC-P2

A NOVEL AND GREEN ANALYTICAL METHOD FOR THE DETERMINATION OF SORBIC AND BENZOIC ACID IN FOOD BY CAPILLARY ION CHROMATOGRAPHY WITH CONDUCTIVITY DETECTION

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An innovative and green analytical method for the simultaneous determination of two food preservatives, sorbic acid (SA) and benzoic acid (BA), by capillary ion chromatography with conductivity detection, is presented. After optimization of alkaline hot extraction, purification procedure and chromatographic conditions, the method was validated, with excellent results in terms of linearity ($R^2 > 0.999$), recovery values (ranging from 90.2% to 105.8%), limits of detection and quantification (1.6 and 4.1 mg kg^{-1} and 4.9 and 12.6 mg kg^{-1} for SA and BA, respectively) and precision (CV% lower than 3.9). The method was applied to all food and beverage types in which the addition of these food preservatives is permitted, according to European regulations, successfully. The method proved to be flexible, highly sensitive and selective, accurate and robust. Finally, embracing the main principles of Green Analytical Chemistry and the challenge of greening laboratory practices, the proposed method can be considered environmentally friendly, sustainable and “reagent-free”[1].

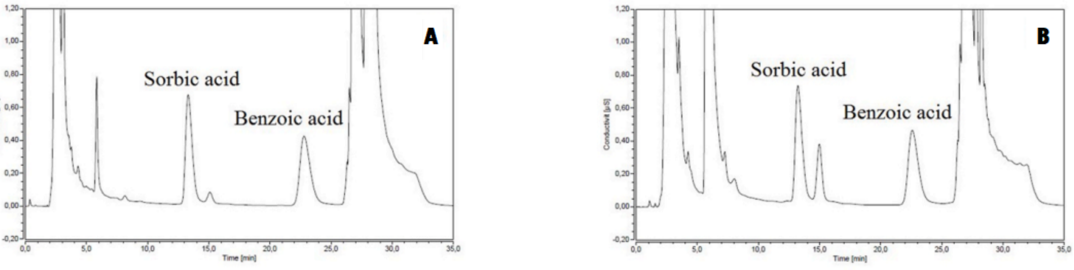

Figure 1: Chromatogram examples. Samples fortified with 1000 mg kg^{-1} of sorbic and benzoic acids: (A) Peach jam, (F) Vegetable soup

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Acknowledgements:
The participation to the XXX Conference of the Analytical Chemistry Division was possible thanks to the research project code IZSPB 07/20 RC, financed by the Italian Ministry of Health.

GC-P3

GREEN EXTRACTION OF POLYPHENOLS FROM FRUIT WASTE AND POSSIBLE USES OF EXTRACTS IN COSMETIC FORMULATIONS

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The processing of agricultural products inevitably leads to large amounts of waste, which is a serious disposal problem. Most of the waste is recycled as animal feed and compost, but large quantities remain. In particular, the fruit and vegetable supply chain results in approximately 90 million tonnes of residues per year in Europe, a volume that is expected to increase in the coming years[1]. For example, a large part of the total berry production is processed for juice production, of which approximately 20–30% ends up as waste[2]. Additionally, a large amount of fruit is wasted in the field due to unforeseen weather conditions exacerbated by climate change. In the case of cherries, for example, this leads to losses of 6% in the field (according to 2022 Istat data) due to biotic and abiotic factors, in particular cracking, that irreparably affects the commercial characteristics. In a circular economy approach, also considering the high value due to the presence of active compounds, it is crucial to recover fruit wastes, rich in phenols and active substances[3]. Taking into account the principles of "green chemistry," the development of a polyphenol valorization process requires the identification of environmentally friendly solvents[4]. Given the lower extraction capacity of natural solvents compared to organic ones, the study of new extraction methods is being investigated. From this perspective, polyphenolic extracts obtained by green approach can be used as active agents (antimicrobial and antioxidant) in cosmetics and packaging. The aim of our work was to evaluate different green solvents for the extraction of bioactive compounds. The solvents studied were NADES: composed of two or more natural components such as organic acids, amino acids, or sugars. The microwave-assisted extraction (MAE) technique was used to improve the extraction yield and extraction conditions were optimized using a DoE approach. Finally, the results of the NADES extraction were compared with those of the organic solvent extraction. The extract obtained will be used as an active antioxidant agent in a cosmetic formulation developed in collaboration with the CTF (Chemistry and Pharmaceutical Technologies) department. Stability analyses will be carried out on the final product and the antioxidant capacity will be tested.

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Poster Chemiometria

CH-P1

RAMAN HYPERSPECTRAL IMAGING AND CHEMOMETRICS: A TOOL FOR THE STUDY OF PYRITE WEATHERING PRODUCTS

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This study develops a novel methodology based on chemometrics and Raman hyperspectral imaging for the analysis of chemically heterogeneous surfaces of weathered minerals[1]. The validity of the approach has been tested on a pyrite sample (figure 1) showing different alteration products. A preliminary exploratory analysis is conducted by means of *Principal Component Analysis* (PCA) in order to identify and discriminate between minor a major Raman features. After the splitting of the initial dataset, *Multivariate Curve Resolution-alternating least squares* (MCR-ALS)[2] was carried out for the analysis of major components, proposing two different alternatives depending on whether a Raman library is available or not. Three diverse components were found, corresponding to pyrite and hematite vibrational modes, as well as features of an amorphous alteration product patina. Moreover, for the analysis of the minor weathering phases, *K-means clustering* was performed and groups of similar pixels of low variance were identified and related to their respective centroids, revealing the presence of sulfates. This methodology enables a semi-quantitative threshold-based characterization of chemical features, providing a visual representation of the phase distribution on the surface of the sample.

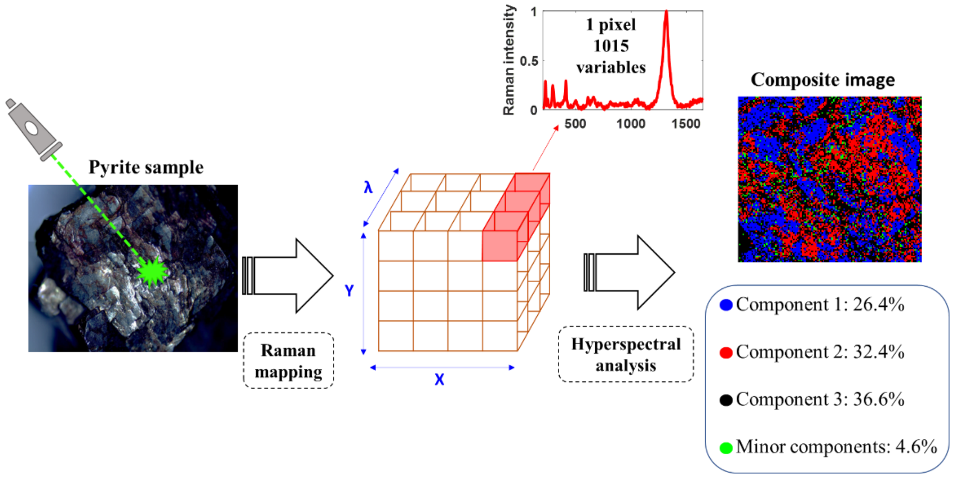

Figure 1: Scheme of the approach proposed in the study.

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CH-P2

NEAR-INFRARED FINGERPRINTING STUDY OF LICHEN THALLI FOR DISCRIMINATING CHANGES IN LICHEN COMMUNITIES

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Near-infrared spectroscopy (NIRS) is an accurate, fast and versatile technique whose full potential remains to be exploited.

Lichens are excellent bioindicators of air quality. The identification of changes in biodiversity and damage caused by pollutants on thalli is laborious and requires highly qualified personnel, hindering its implementation in routine environmental monitoring[1].

The aim of this work is to find out whether NIR global molecular fingerprints can help in discriminating changes in lichen communities. In order to reach this goal, 195 lichen samples belonging to different locations, to different species, and subjected to different levels of damage have been analysed using an ASD LabSpec® 4 Standard-Res laboratory analyzer in the range 350 -2500 nm with a reflectance probe.

In the NIR range, water has a specific spectral pattern that changes with perturbations.

In this study, we focus on the first O-H overtone (1300–1600 nm) of the NIR spectra because this is where most water bands are identified[2].

Principal Component Analysis (PCA) was performed on the spectra pretreated with multiplicative scatter correction (MSC) after mean centering.

In conclusion, NIRS fingerprinting combined with chemometrics is revealed as an extremely fast and versatile tool for the study of differences between lichen thalli and to evidence changes in lichen communities, and also for the study of phenotypical changes induced by the environment.

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Acknowledgements:
We would like to thank for funding PROMETEO/2021/005.

INVESTIGATING MULTIVARIATE SOURCES OF UNCERTAINTY: A CRUCIAL STEP FOR SPECTROSCOPIC METHOD DEVELOPMENT

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In recent times, there has been a growing interest in NIR handheld and miniaturized devices coupled with chemometrics, primarily due to their affordability, utility in various applications and their alignment with green analytical chemistry principles[1]. Since the instrumentations are quite new, studying the sources of uncertainty in raw data could be useful for improving analytical set-up, technologies, and data management[2]. Attention is needed on the entire analytical protocol, from sampling to data modelling, through data collection and processing. The limits of analytical methods are related to the types of error included in the data, so the importance of investigating the error structure in raw data could be crucial[3]. This study serves multiple purposes and proposes a practical and feasible methodology for investigating multivariate uncertainties in raw data and emphasizes the need to evaluate measurement errors for optimizing any analytical method. Spectra were acquired on samples with different chemical and physical characteristics by considering different acquisition parameters, types of replicates, and various acquisition configurations or NIR instrumentations[4]. A compelling example of how understanding the sources of errors in raw data can enhance the quality of measurements is furnished. Additionally, investigating uncertainties for data handling and instrumental performance monitoring is addressed. Insights were gained about the impact of sample compactness on the multivariate errors in external dispersive NIR reflectance spectra.

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CH-P4

CLASSIFICATION OF LIGANDS' EFFECT ON STABILIZATION OR DISRUPTION OF G4 STRUCTURE BASED ON CD SPECTRA

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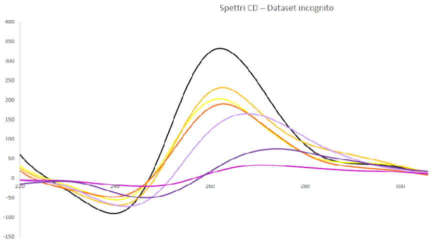
G-quadruplexes (G4s) are secondary structures of nucleic acids formed in genome regions rich in guanines and recognized as key structural elements for the regulation of different biological processes[1]. Four guanines can associate to form square planar structures called *guanine-tetrads*, that can stack on top of each other to form the backbone of G4s[1]. Among distinctive features, G4s can adopt different topologies that are due to the direction in which nucleobase strands proceed, described as parallel, antiparallel, or hybrid[2]. G4s' topologies can be easily identified by their unique dichroic signal, therefore CD spectra are currently used to assess the effect of novel ligands, acting at modulating the G4-folding, on wild-type G4s topologies. In the present research, we evaluated the effects of stabilizing and destabilizing G4-ligands on a novel G4 recently discovered by us in the Apolipoprotein E promoter region (Figure 1). The entity of the interaction is qualitatively evaluated by comparison with a restricted library of reference structures, surely assigned to parallel, antiparallel, and hybrid (Figure 2). We show how PCA, obtained by centring, and not autoscaling, CD spectra can successfully be employed to visualize the effect of different ligands in a more accurate way that what done by previous studies. Moreover, on this base, a SIMCA classification[3] was applied to model parallel, hybrid and antiparallel classes, exploiting the reference dataset to train the models to recognise the distinctive features of G4 topologies of interest, becoming a promising tool to measure the effect on G4 structures.



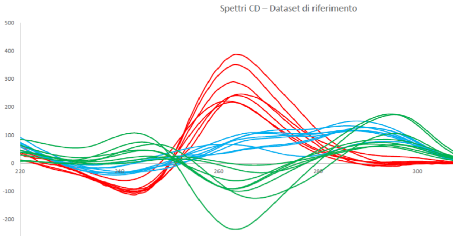


Figure 1: Effect on CD spectra obtained after interaction with different ligands on an original parallel structure, here reported in black. Figure 2: Reference CD spectra of parallel, in red, antiparallel, in green, and hybrid, in ciano of G4 structures.

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LOCAL ROBOOST PLS IMPLEMENTATION AND EVALUATION

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A novel RoBoost PLS algorithm has been recently proposed[1] to assess the relevance of different samples in PLS calibration based on a weighting scheme which considers outlying behaviours with respect to X-residuals, Y-residuals, and leverage. The method (extended also to multiple responses) was found to successfully detect outliers in both the X- and Y-space, thus, improving the quality of the final regression models. In this work, we present an extension of this methodology to the local regression framework[2], as well as to multiblock-PLS regression. In particular, we will consider two situations: the first in which samples are outliers with respect to the overall data set, and the second in which they are outliers with respect to a local subset. Different scenarios in terms of data structure will also be investigated: the presence of clear groupings and smooth transitions (as in process monitoring) in X, as the presence of non-linearities in the X-Y relationships, *etc*. In these cases, local regression is best suited with respect to standard regression, but the influence of outlying samples may be of different nature and, therefore, distinct should be the solutions to be adopted for preserving model robustness.

The developed methodology will be tested on simulated spectral data[3] and in real case-studies from the chemical process industry.

In the local-Roboost algorithm several parameters need to be tuned since two weighting schemes are combined (the Roboost and the local). For this purpose, a double cross-validatory procedure is resorted to. The local-Roboost code has been developed in MATLAB environment.

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CH-P6

APPLICATION OF IR SPECTROSCOPY AND CLASS-MODELING TECHNIQUE FOR ALMOND TRACEABILITY

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The aim of this study was to develop a model for determining the geographical origin of various almond varieties produced on Italian soil, given the high economic interest due to numerous export requests, as well as the development of a model capable of preventing potential food fraud. In detail, a model has been developed for the classification of the geographic origin of one of the most common varieties of almonds cultivated and sold in different Italian regions renowned for their production, namely Apulia (South Italy), Calabria (South Italy) and Sicily (South Italy). A food traceability investigation was then conducted on Prunus Amygdalus, also known as Prunus Dulcis, the seed of the tree belonging to the Rosaceae family (genus Prunus). The analytical technique used for almond analysis was ATR FT-IR spectroscopy, rapid and green techniques technique. IR spectra were acquired both on the almond shell and the edible seed in order to accurately classify almonds from Apulia (South Italy), Calabria (South Italy) and those from Sicily (South Italy), as well as differentiate between harvest years (2021 and 2022). The spectroscopic data obtained from this analysis were analyzed using exploratory analysis techniques, including Principal Component Analysis (PCA), followed by a Class-Modeling technique applying the Soft Independent Modeling of Class Analogies algorithm (SIMCA)[1]. Based on the results obtained from the chemometric analysis, it was possible to classify the almonds according to their geographical origin with high efficiency. The built SIMCA classification model demonstrated that it is possible to distinguish almonds from the Apulia (South Italy), Calabria (South Italy) and Sicily (South Italy) regions, achieving acceptable classification efficiency percentages (better for almond shells compared to the values obtained for the edible seeds). In conclusion, the model developed in this study was able to accurately determine the class membership and, therefore, the different geographical origin of the studied almond variety. This opens the way for future applications of similar models. Furthermore, this approach could be extended to other varieties of dried fruit for further characterization and classification studies.

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CH-P7

CHEMOMETRIC APPROACH FOR THE STUDY OF ANTI-OXIDATIVE ACTIVITY OF WATER-BASED EXTRACTS OF CHAMOMILE (*Matricaria chamomilla* L.)

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Chamomile (Matricaria chamomilla L.) is a medicinal plant known for its various beneficial properties, such as anti-inflammatory, antiseptic, analgesic, antimicrobial, antispasmodic, and sedative effects. The plant contains polyphenols[1], including phenolic acids and flavonoids, which contribute to its antioxidant activity and overall health benefits by reducing oxidative stress and inflammation. This study aims to optimize a water extraction method on chamomile flower heads to obtain an aqueous extract with anti-inflammatory and antioxidant properties. A Design of Experiments (DOE) was used to define 27 experiments in which the effects of temperature, time, and amount of chamomile were investigated at three levels (15-25-35°C, and 32-62-92 min and 0,5-1,5-2,5g). The extracts obtained in each DOE point were analyzed using UV-Vis spectrophotometry to study their spectral characteristics and DPPH assay to determine the antioxidant activity of the extracts. The DPPH assay evaluates the ability of antioxidants to reduce the violet-colored DPPH radical, resulting in a color change from violet to pale yellow. The extent of the color change can be related to the antioxidant capacity of the extract. The highest antioxidant activity was observed for the highest amount of chamomile (2.5g) extracted for the lowest time (32 min) and both at the lowest (15°C) and highest (35°C) temperature level, showing a significant decrease in absorbance against the DPPH blank (91,7% and 91,3% respectively). Conversely, the lowest antioxidant activity was found for the lowest amount of chamomile, lowest temperature, and highest time (0,5g, 92 minutes, 15°C), showing a 25,4% absorbance decrease. The DOE approach provided a reliable empirical model describing the relationship between the experimental variables and the response, as witnessed by a high adjusted R^2 value (0,97) and adjusted Q^2 value (0.94) in cross-validation. The study was expanded by the interpretation of the results through the chemometric analysis of the UV-Vis spectra of chamomile extracts by means of ANOVA Simultaneous Component Analysis (ASCA).

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SINGLE-MOLECULE DETECTION OF SARS-CoV-2 SUBGENOMIC mRNAs.

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Several detection approaches and genome sequencing methods have been utilized for SARS-CoV-2[1]. Currently, the SARS-CoV-2 diagnosis is based on Reverse Transcription-quantitative Polymerase Chain Reaction (RT-qPCR) method, which is considered the gold standard. However, the RT-qPCR major limitation is the non-specificity in the detection of genomic, subgenomic, or degradation products of the viral RNA, which can be used as a significant epidemiological marker for detecting different SARS-CoV-2 strains[2,3]. In this study, we evaluated the application of the Single Molecule with a Large Transistor (SiMoT) technology[4] to perform the early detection of nucleocapsid protein coding SARS-CoV-2 sgmRNAs. Preliminary analysis has been accomplished on a specific single-strand DNA that codify for the nucleocapsid (N) protein. The sensing measurements with spiked buffer standard solutions of the target analyte have been carried out with SiMoT platform. Furthermore, the selectivity of the platform has been evaluated through the negative control experiments, registered by exposing the SiMoT biofunctionalized gate to a non-bounding microRNA sequence. The latter experiments allowed to define the Limit of Detection (LOD) of the assay. Three features have been taken as the characteristic elements of each sensing assay, and have been calculated from the whole electronic raw dataset. Those features have been engaged on the development of unsupervised multivariate statistical analysis, the Principal Component Analysis (PCA). The latter has been performed to accomplish outliers detection and highlight graphical clustering of the sensing and negative control data. Moreover, a classification approach based on Linear Discriminant Analysis (LDA) has been undertaken to classify SARS-CoV-2 positive and negative samples.

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CH-P9

CHEMOMETRIC-BASED PREDICTION OF LC−MS RETENTION TIME FOR PESTICIDES

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The retention time (t_R) of chromatographic separations in LC−MS experiments can provide supplementary information to MS/MS spectra for molecular identification. As a result of the high correlation between t_R and molecular structure, it can be used as a filter to eliminate false positives and improve accuracy of annotation[1]. Moreover, t_R is a valid add-on to eliminate unlikely structures in high-resolution mass spectrometry (HRMS).

Retention time of chemical compounds can be foreseen by means of chemometric strategies and Quantitative Structure Activity Relationships (QSAR) approaches, which use empirical models to predict experimental properties (such as t_R) from the molecular structure of compounds.

We retrieved 492 experimental values of t_R, associated with the chemical structure of the corresponding compounds (pesticides), from two different studies[1,2]. Retention time was experimentally measured with different conditions (SFC in high-resolution and unitary low-resolution, with the same mobile phase but different stationary phases). Therefore, thousands of molecular descriptors were calculated and used to develop chemometric models for the prediction of t_R.

Descriptors were selected trough supervised approaches and models were validated with classical protocols (training/test splitting), giving reasonable performances on the test set (Q^2 equal to 78%). Furthermore, we also tried to stress the model application and see the accuracy when predicting t_R of test chemicals measured with experimental conditions different from those of training chemicals. Even in this case, taking into consideration only molecules included in the applicability domain, models were able to predict t_R with adequate accuracy (Q^2 equal to 74%).

Finally, further diagnostics were carried out exploring the chemical space with chemometric tools to understand which structural features were associated to highest residuals, that is, which classes of compounds are mostly related to errors in the retention time prediction.

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CH-P10

PoliBrush – AN EDUCATIONAL SOFTWARE FOR THE MULTIVARIATE PROCESSING OF SPECTRAL IMAGES

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Since the first introduction of hyperspectral imaging in chemistry, the need for dedicated software was recognized by the chemometric community. Nonetheless, considering that such an introduction has been relatively recent, availability of software for multivariate analysis of hyperspectral images is still limited, if compared with general chemometric applications. PoliBrush is a freely distributed, stand-alone software designed for teaching exploratory multivariate analysis in the frame of color RGB and spectral imaging. PoliBrush implements principal component analysis (PCA) as its core method. It features a single main window that provides users with essential tools for spectral image preprocessing and exploration. The software emphasizes an interactive brushing approach, enabling users to gain a comprehensive understanding of the relationships between PCA score space and image pixel space. PoliBrush usage and its operational procedure will be demonstrated through two case studies, whose data will be made available for download. The software has already been successfully used in various educational settings and workshops on multivariate approaches for spectral imaging, proving its effectiveness in teaching key concepts.

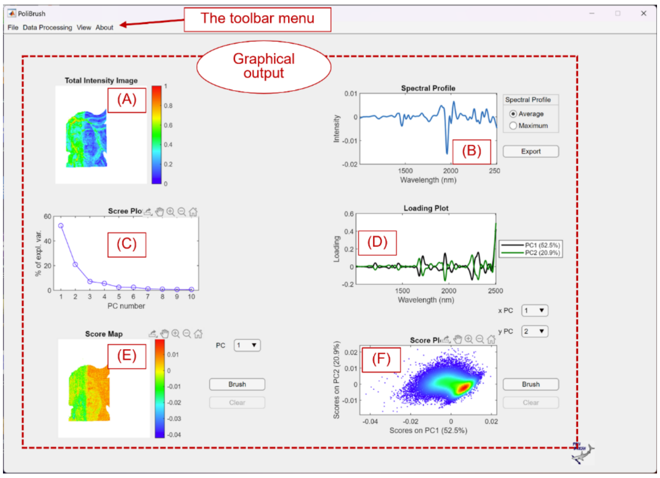

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Figure 1: Main window of PoliBrush with graphical output panels: total intensity image (A), average/maximum spectral profile (B), PCA scree plot (C), loading line plot (D), score map (E), and score scatter plot (F).

Acknowledgements:
Financial support provided 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.

Poster Spettroscopia

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) MEASUREMENTS TO INVESTIGATE THE ORGANIC ADDITIVES CONTENT IN COMMERCIAL PLATING BATHS

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Organic additives in commercial plating baths are essential to obtain desired deposit properties such as improved adhesion, hardness, appearance, and corrosion resistance. However, maintaining optimal concentrations of these additives is crucial because they can degrade and drag-out, so they have to be frequently monitored and dosed. Conventional chromatographic methods for quantifying organic additives suffer from drawbacks such as time-consuming sample preparation and high costs, therefore they are not typically used in industrial field. Electrochemical methods represent a reliable alternative, allowing quantitative analysis considering the effects the additives exert on the electrodeposition rate, regardless of their chemical composition and providing, at the same time, practical information about the condition of the bath. We performed Cyclic Voltammetric Stripping (CVS) measurements on a commercial acid copper plating bath to determine the concentrations of the three main additives used in these baths: suppressor, brightener and leveller. This procedure represents the state of the art[1], but it appears to be time and reagents-consuming and do not always provide accurate results. We also conducted Electrochemical Impedance Spectroscopy (EIS) experiments using a $10^5 - 10^2$ Hz frequency range. This technique enables the electrodeposition process to be described in terms of resistive and capacitive components and correlated with the concentration of each organic additive. The measurements were performed in a three-electrode cell, at 30 °C on a wide range of samples for a statistical processing of the results. The resultant model was then applied to the study of real samples, obtaining promising results. The application of EIS in the galvanic field is of great interest both from an industrial and academic point of view because it makes it possible to follow the aging of the bath[2] and to fully understand the role and the interaction of each additive during the electrodeposition process by obtaining accurate results with a single measurement on a real sample.

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A SPECTROSCOPIC AND ELECTROANALYTICAL STUDY OF SINGLE-ION CATALYSTS FOR THE OXYGEN REDUCTION REACTION

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Oxygen Reduction Reaction (ORR) plays a key role in the energy sector, particularly in the development of energy storage and conversion systems like fuel cells. This reaction can take place via two main pathways: direct reduction to water, or intermediate reduction to hydrogen peroxide[1]. Hydrogen peroxide is a corrosive product that significantly reduces the efficiency of alkaline fuel cells. Consequently, there is a pressing need to minimize its formation by developing catalysts with enhanced performance. For this reason, accurate quantification of the hydrogen peroxide generated during the reaction is essential to assess the catalytic activity of electrocatalysts[2]. In this study, we present the characterization of Single-Ion catalysts based on carbon nanotubes functionalized with Pd(II) complexes, which exhibit remarkable catalytic activity and show low hydrogen peroxide production. The catalysts were thoroughly analyzed using advanced spectroscopic techniques, namely Scanning Electron Microscopy coupled with an Energy-Dispersive X-ray detector (SEM-EDX), X-Ray Diffraction (XRD), and X-ray Photoelectron Spectroscopy (XPS). These techniques provide valuable information on the structural and chemical properties of the catalysts, elucidating their composition, morphology, and electronic states.In addition, we used Rotating Ring-Disk Electrode (RRDE) electrochemical technique to evaluate the performance of the catalysts in the Oxygen Reduction Reaction. Our results demonstrate that the tested materials catalyze the four-electron reaction pathway, minimising the formation of hydrogen peroxide.These results set the stage for future advances in the development of effective catalysts for alkaline fuel cells. By reducing the amount of expensive platinum group metals (PGMs), our Single-Ion catalysts offer a promising alternative to improve the efficiency and reduce the cost of ORR catalysts.

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S-P3

COLOR ASSESSMENT USING EVERYDAY TOOLS: CAMERA AND SMARTPHONE FOR COLOR EVALUATION

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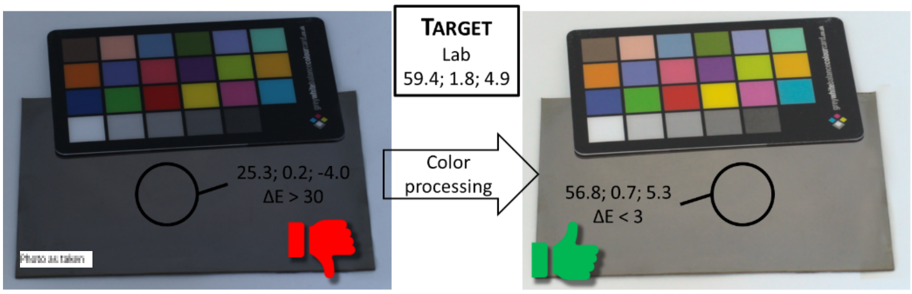
Color assessment is vital in industrial applications, especially decorative electroplating. Surface deposits on manufactured goods must meet colorimetric standards[1]. Spectrophotometers are commonly used to evaluate color using the L*, a*, and b* parameters in the CIELAB color space[2].

In addition to conventional methods, colorimetric coordinates can also be obtained by capturing images using a digital camera or smartphone, along with colorimetric references and specialized image processing software. The colorimetric references aid in adjusting and enhancing the captured images to obtain accurate colors, ensuring that the acquired information represents the object's color realistically, irrespective of lighting conditions[3]. Upon reprocessing, the colorimetric coordinates L*, a*, and b* can be obtained. This study aims to perform and compare colorimetric measurements using a UV-Vis spectrophotometer, a portable spectrophotometer, a digital camera, and a smartphone. Samples comprising various finishes achieved through galvanic deposits of gold, palladium, rhodium, and/or their alloys were measured.

The colorimetric coordinates obtained from each instrument mentioned above were compared to evaluate the feasibility of facilitating colorimetric determination, particularly in industries where advanced instruments like spectrophotometers are often unavailable.



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S-P4

INVESTIGATION OF COLOUR VARIATIONS IN CrO_x PVD COATINGS: EFFECTS OF OXYGEN-TO-ARGON RATIO AND SPUTTERING DEPOSITION TIME

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This work focuses on the investigation of colour variations in CrO_x PVD (physical vapor deposition) coatings deposited on a brass substrate. The study examines the influence of two key parameters, the oxygen-to-argon ratio and the deposition time, on coating colour. The deposition process employed magnetron sputtering[1]. The research methodology involved systematically varying the oxygen-to-argon ratio within the sputtering gas mixture and adjusting the sputtering deposition time. The resulting coatings on the brass substrate were subjected to comprehensive surface and chemical characterizations, including EDS-SEM (Energy-dispersive X-ray spectroscopy and scanning electron microscopy), XRF (X-ray fluorescence) and UV-Vis reflectance. The EDS-SEM analysis provided valuable insights into the morphology and elemental composition of the coatings on the brass substrate, while XRF analysis offered quantitative measurements of the elemental composition. UV-Vis reflectance measurements were utilized to analyse the optical properties, including colour, of the coatings on the brass substrate. The experimental results revealed significant colour variations in the CrO_x PVD coatings on the brass substrate, depending on the oxygen-to-argon ratio and the sputtering deposition time. These parameter changes influenced the thickness, composition, and crystallinity of the coatings, leading to variations in coloration[2]. The reflectance data assigned the optical properties and colour characteristics of the coatings on the brass substrate. This research contributes to the fundamental understanding of colour generation mechanisms in chromium oxide coatings on brass substrates. The comprehensive characterization techniques employed in this study offer a deeper understanding of the microstructure, elemental distribution, and stability of the coatings on the brass substrate. The knowledge gained from this investigation paves the way for the development of advanced coatings with improved colour control and aesthetics, ultimately enabling their application in various fields, including architecture, automotive, and decorative industries.

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S-P5

SIMPLE COLORIMETRIC ASSAY BASED ON POLYMERS NANOFILMS FOR GOLD DETECTION

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Surface coating is an important task in material sciences that has stimulated an impressive variety of interests and significant efforts devoted to the development of efficient, simple, and material-independent surface modification strategies. In this context, thanks to their simplicity (self-polymerization under alkaline conditions), versatility (to form adherent film onto a variety of surface) and secondary reactivity (to induce electron transfer), catecholamine polymers (polydopamine, PDA and polynorepinephrine, PNE), have been widely explored as surface modifiers of several materials[1,2]. Among the vast use of these polymers in many fields, part of literature also reports on application taking advantage of the redox potential of the catechol/quinone moieties[3]. This reducing power could be applied towards metallic ions to form metallic nanoparticles (NPs). Inspired by DA and NE, also serotonin (SE), was very recently investigated. SE has a similar structure to DA and is self-oxidized and polymerized to polyserotonin (PSE) in alkaline solution as well[4].

On this basis, in this presentation, we report the modification of disposable ELISA plates with three different nanofilms of PDA, PNE, and PSE for the Au quantification in aqueous solutions. All the three polymers were able to spontaneously reduce Au cations to originate gold nanoparticles (AuNPs) at their surface, allowing a UV-Vis spectroscopy measurements, thanks to AuNPs Localized Surface Plasmon Resonance (LSPR), obtaining a calibration curve for Au in standard solution. As a proof-of-concept of such analytical method applicability, we analyzed several matrices, aiming to develop fast, low cost and simple analytical approaches to monitor Au content.

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S-P6

SYNERGISTIC NANOANTIVIRALS COMBINING TWO BROAD-SPECTRUM METALS: THE CASE OF ZnO/AgCl NANOMATERIALS

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The development of novel antiviral materials has become one of the most investigated areas in the nanoantimicrobials field, after the outbreak of the severe acute respiratory syndrome coronavirus (SARS-CoV-2)[1]. Nanomaterials containing bioactive metal species such as silver and zinc exhibit antimicrobial properties against a wide range of microorganisms, providing significant support in the fight against pathogen diffusion. In the past decade, we have studied green water-based and scalable electrochemical routes for the production of zinc oxide nanostructures (ZnO NSs) with enhanced activity towards different pathogens, including SARS-CoV-2[2]. More recently, a green, scalable and reproducible argentometric titration was successfully used to develop antimicrobial silver chloride nanoparticles (AgCl NPs) capped by benzyl-hexadecyl-dimetylammonium chloride (BAC)[3]. In order to further exploit the broad-spectrum efficacy of silver- and zinc-based NAMs, their synergistic combination into a novel nanostructure is proposed in this contribution. Electrosynthesized ZnO NSs capped by BAC were decorated by AgCl NPs stabilized by the same surfactant, along with other antimicrobial salts. The results of microscopy (TEM) and spectroscopy (UV-Vis, ATR-IR, XPS) analyses will be discussed, offering an overview of the materials structure, composition and surface reactivity. In addition, the antimicrobial properties will be reported and interpreted based on ionic release properties of the investigated materials, thus providing a rationale for the antiviral efficacy.

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Acknowledgements:
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S-P7

INSIGHTS ON PLASTICS FRAGMENTATION PROCESS IN MARINE ENVIRONMENT BY AN X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) STUDY

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Plastics have conquered almost every area of our lives and can be found in numerous every-day items, from cosmetic and hygiene articles to foodstuffs[1]. They are synthetic organic materials, characterized by a high degree of chemical resistance, considerable plasticity as well as versatility of performance and ease of processing. All these properties have led to the immoderate use of plastic materials with their subsequent release into the natural environment and accumulation especially in marine ecosystems[1,2]. Despite their resilience and resistance, plastics can undergo fragmentation processes by physical-chemical and biological agents, producing microplastics (MPs) or even nanoplastics (NPs), with consequences for organisms that populate environmental compartments. However, determining the fate of plastics materials in the environment is inherently difficult, both because the timescale of degradation and the dynamics of these processes are not clear and grey areas remain. It is well known that the fragmentation process originates from oxidation and hydrolysis of plastic materials, by solar radiation (especially the UV portion), water hydrodynamics and the activity of aquatic organisms[1].

In this work, we propose the use of the X-ray Photoelectron Spectroscopy (XPS) technique for chemical characterization of different plastic materials, namely polystyrene (PS) and polyethylene (PE), before and after a weathering treatment under simulated environmental conditions, to monitor surface oxidation/hydrolysis processes and possibly correlate to plastics fragmentation. In brief, plastic standard samples (pellets with a size of around 1 cm^2) are artificially weathered in a closed chamber at fixed temperature (25 °C) and relative humidity (50%), under the exposure to controlled UV radiation (UV-A: 13.6 W/m^2 and UV-B: 3 W/m^2) in ultra-pure and marine water in hydrodynamic conditions (under stirring, 400 rpm) for different time intervals (1, 3, 7, 14, 30, 60 days). Preliminary XPS results show that proceeding the treatment, there is an increase of oxygen-containing functional groups (namely, C-O, C=O and O-C=O) on the plastics surface suggesting a partial degradation of the polymeric materials, under the adopted conditions. The effect of marine water in such a process emerges from the comparison with results on plastic in ultra-pure water, as well as the effect of UV light is suggested by the comparative XPS analysis of plastic samples kept at dark for the same time intervals.

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Acknowledgments:
The activity was funded by the “I-plastic” project (JPI Oceans), CUP: F85F18002370005

S-P8

INVESTIGATION OF HEAVY METAL ADSORPTION ON PLASTIC MATERIALS IN MARINE WATER BY X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

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Plastic pollution has become one of the most pressing environmental issues, due to the inefficient or nonexistent waste management[1]. In nature, plastics can undergo a multitude of processes by chemical/physical and/or biological agents producing a change in their initial composition. In some cases, hazardous compounds can adsorb on the surface of plastic materials that could act as vectors with dangerous effects on the biological communities living in marine environments and therefore also to humans[1]. Among these contaminants, heavy metals (HM) are widely known for their negative long-term effect on the living organisms such as cancer, nerve damage, failure of the liver, kidneys and even death[1]. However, the dynamics of their interaction with plastics are still unclear, although the adsorption of heavy metals seems to occur almost universally on plastics regardless of their composition. In particular, it appears to be higher in weathered plastics[2], probably due to the presence on their surface of oxygen-containing functional groups, acting as binding sites[2] and making the surface more hydrophilic.

Herein, we propose to use X-ray photoelectron spectroscopy (XPS) to obtain chemical information about the adsorption process of different heavy metals (Pb^{2+}, Hg^{2+} and Cd^{2+}), on commonly used plastic materials (polyethylene terephthalate, PET, polyethylene, PE and polystyrene, PS). Standard plastic samples (size of 1 cm^2) are exposed to heavy metals solutions (0.5, 5 and 50 $mg \cdot L^{-1}$), prepared in ultra-pure and marine water for different time intervals (1 day and 7 days) in hydrodynamic conditions (stirring at 400 rpm). Preliminary XPS results show an increase in heavy metals adsorption on plastics with concentration and time exposure, as expected, as demonstrated by the atomic ratios between the heavy metal signal and C 1s (used as reference). The possible difference adsorption mechanism in ultra-pure and marine wateris in progress, supported by metal speciation studies. Moreover, metals adsorption experiments that involve the use of UV weathered plastics are planned for better simulating environmental conditions.

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Acknowledgement

The activity was funded by the "I-plastic" project (JPI Oceans), CUP: F85F18002370005

S-P9

AN ANALYTICAL APPROACH FOR CLARIFYING THE FATE OF IRON IN PRESENCE OF CITRATE IONS IN CONTACT WITH NI-FREE STEEL

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Ni-free DIN 1.4456 stainless steel is a suitable material for orthodontic applications due to its good biocompatibility and corrosion resistance. Usually, the corrosion studies are performed *in vitro* by using model saliva solutions, that simulate the real human saliva[1] such as the saliva formulation known as Tani-Zucchi (T-Z) that consists of inorganic salts, such as chlorides, phosphates, thiocyanates and only urea as organic component[1-3]. The organic compounds present in saliva might play an important role in the stability of surface films and on the dangerous release of metal ions, as reported for brass[4,5]. The aims of this work were the development and the optimization of an analytical method for clarifying the fate of iron in presence of citrate ions in contact with Ni-free DIN 1.4456 A model saliva solution, Darvell (D)[6], which contains trisodium citrate and other different organic compounds such as urea, uric acid and lactic acid, was used. The analytical method was developed combining electrochemical *in-situ* techniques with the X-ray photoelectron spectroscopy (XPS) *ex-situ* technique. Periodic calibrations according to ISO 15472:2014 were performed and reference compounds were analysed to ensure accurate qualitative and quantitative analysis. The Fe to Cr atomic ratio diminishes upon exposure time (Figure 1) indicating a progressive chromium enrichment in the surface film. This finding can explain the decrease of the corrosion rate of DIN 1.4456 stainless steels in contact with D solution. The chromium enrichment corresponds to an iron depletion, this might be due to the complexation of iron in the solution by the presence of citrate ions. The analytical approach of this work is well suited for understanding the mechanism of the film formation in Darvell solution.

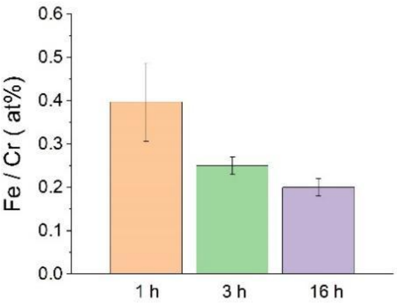

Figure SEQ Figure * ARABIC 1: Fe/Cr atomic percentage ratio on steel exposed 1 h, 3 h and 16 h to D solution.

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Acknowledgements: The financial support of the European Union NextGenerationEU under the National Recovery and Resilience Plan (NRRP) of Ministero dell'Università e della Ricerca (MUR) (Project code PE0000021, "Network 4 Energy Sustainable Transition, NEST) is acknowledged.

Poster

Spettrometria di Massa

MS-P1

OPTIMIZATION OF A NEW GC-MS BASED METHOD FOR IDENTIFYING AND QUANTIFYING MULTICLASS POLLUTANTS IN BIOLOGICAL MATRICES: A POWERFUL TOOL FOR HUMAN BIOMONITORING

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Environmental research and public health in the 21st century look toward numerous challenges including the widespread use of substances that are potentially harmful to humans. Among the several anthropogenic pollutants present in the environment, persistent organic pollutants (POPs) are the most concerning compounds due to their potential toxic effects. However, the restriction has led to the introduction of new chemicals now called "emerging contaminants" (ECs). The urgent need to get a complete view of everyone's exposome meets the necessity to assess how and how much chemicals are actually absorbed from the environment into the organism itself, and whit the practical question of the methodology applied to measure the exposome itself. In this context, Human Biomonitoring (HBM) plays a crucial role in establishing exposure and risk assessment.

With the aim to contribute to the comprehensive characterization of the exposome, we developed and validated a new gas chromatography-mass spectrometry method for assessing the identification and quantification of a broad spectrum of POPs and ECs in biological matrices. Using a Design of Experiments (DoE) concept, a highly sensitive MS assay was developed for the quantification of the interested compounds in serum and non-invasive matrices. Critical method aspects such as the extraction procedures, chromatography separation, and method sensitivity were comprehensively optimized starting with the most studied compounds to those less investigated in the literature.

The proposed methods were validated to achieve high analytical performance in terms of selectivity, linearity (R2 >0.995), accuracy (bias%≤ 10%), precision (CV%≤ 10%), robustness, ruggedness, limit of detection, limit of quantitation, recovery, matrix effect, and repeatability according to the international guidelines.

The developed method represents a powerful tool that can be employed in HMB to investigate the impact of pollutants on human health expanding the still limited knowledge about the potential use of non-invasive matrices. This method will be useful in future applications on subjects at high risk of exposure to assess potential correlations between pollutant levels and disease development.

Acknowledgements:

This work was supported by the European Union NextGenerationEU from Piano Nazionale di Ripresa e Resilienza (PNRR) - Partenariati Estesi (PE3 - RETURN) - CUP J33C22002840002

VALIDATION OF METHOD FOR THE DETERMINATION OF *ALTERNARIA* TOXINS IN SUNDRIED TOMATOES BY LC-MS/MS

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Alternaria is a genus of fungi which grows on fruit and vegetables, responsible for producing a series of low molecular weight metabolites, named *Alternaria* toxins. In 2011 EFSA expressed its scientific opinion on the risk for animals and public health associated with the presence of these toxins[1]. Later the Recommendation (EU) 2022/553 established the indicative levels for some *Alternaria* toxins in various food products as tomatoes[2]. In this context, an analytical method based on liquid chromatography coupled to tandem mass spectrometry was validated for the determination of five toxins in sundried tomatoes: Alternariol (AOH), Alternariol Monomethyl Ether (AME), Tenuazoic acid (TeA), Tentoxin (TEN) and Altenuene (ALT). These toxins were extracted from the sample with a solution of methanol/water/acetic acid and subsequently an aliquot of the extract was purified on a Strata-XL column. After the elution with methanol, the *Alternaria* toxins were analyzed using a 6500+ QTRAP triple quadrupole spectrometer equipped with an Ion Drive source in negative ion mode. The chromatographic separation was performed with a Kinetex EVO C18 column using 5 mM ammonium acetate buffer and methanol as mobile phases in a gradient program.

The validation was performed according to the performance criteria mentioned by Regulation (EU) 2017/625 and the following parameters were considered: specificity, limit of detection and quantification (LOD and LOQ), linearity, repeatability, reproducibility, accuracy, and uncertainty.[3] LOD and LOQ were respectively in the range of 0.1-0.23 and 0.1-1.3 µg/kg, satisfying the requirements established by European legislation. The recovery rates were between 73% and 104% with a relative standard deviation of intra-laboratory reproducibility below 13%.

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MS-P3

DETERMINATION OF STRESS-RELATED HORMONES IN SHEEP WOOL BY MEANS OF LIQUID CHROMATOGRAPHY COUPLED TO HIGH RESOLUTION MASS SPECTROMETRY: PRELIMINARY RESULTS

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High levels of biomarkers linked with negative emotional state can be an animal health and welfare assessment tool. Cortisol, its metabolite cortisone, dehydroepiandrosterone (DHEA) and its sulfate metabolite (DHEAS) have been taken into account as stress-related hormones[1,2]. The development/validation of a quantitative method for endogenous compounds is challenging because of the difficulty to obtain analytes-free authentic matrices as quality control samples, so surrogate analytes (i.e. cortisone-$^{13}C_3$, cortisol-$^{13}C_3$, DHEA-$^{13}C_3$, DHEAS-$^{13}C_3$) have been used to circumvent the issue. As regards to the method development, after the optimization of LC-HRMS/MS conditions, the experiments have been carried out spiking sheep wool samples with the analytes, using the previously published sample preparation protocol[3]. Preliminary results are promising (Figure) and further experiments are in progress to achieve performance characteristics meeting the requirements of EMA guidelines on bioanalytical method validation.

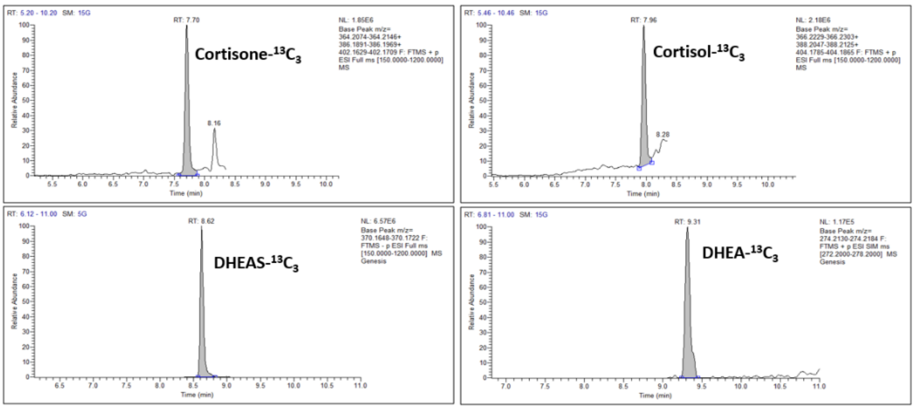

Figure: Chromatograms of the surrogate analytes in sheep wool spiked at 20 pg mg^{-1} (DHEA-$^{13}C_3$ at 400 pg mg^{-1}).

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Acknowledgements - The authors gratefully acknowledge financial support from the Italian Health Ministry ("Towards a fair and sustainable production in marginal areas: novel indicators to improve animal welfare" Ricerca Finalizzata GR-2021-12374382)

MS-P4

EXPLORING PFAS CHEMICAL IONIZATION MECHANISM IN LC-MS: UNDERSTANDING THE KEY PARAMETERS FOR ENHANCED DETECTION

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Per-and polyfluoralkyl substances (PFAS) are a class of synthetic pollutants commonly used in industrial processes and consumer products and dangerous for human health.

This research focused on investigating negative chemical ionization (NCI) as an alternative to conventional techniques for analyzing five selected PFAS: perfluorooctanoic acid, perfluorononanoic acid, perfluorodecanoic acid, perfluorododecanoic acid, perfluorotridecanoic acid.

The CI source of a triple quadrupole mass spectrometer was coupled with a UHPLC system via the liquid electron ionization (LEI) interface. LEI vaporized the analytes conveyed by a suitable acetonitrile (ACN) flow rate before entrance into the MS ion source. The effects of different parameters affecting CI in liquid chromatography-mass spectrometry were evaluated: reagent gases (methane, isobutane, argon, and no reagent gas), presence of formic acid (FA) and water in the mobile phase, ACN flow rate. Water and FA addition were considered because they were necessary for chromatographic separation. PFAS were analyzed in flow injection analysis (FIA); ion source and transfer line temperatures were 150 °C and 350 °C, respectively. The spectra were obtained in full scan acquisition mode with a mass range of *m/z* 92-800. FIA results demonstrated that methane, isobutane, and argon provided similar fragmentation and signal intensity. It was observed that the sole presence of ACN can promote CI, providing low-fragmentation spectra and enhanced sensitivity. The ACN flow rate of 0.2 and 0.4 mLmin^{-1} was split to 0.5 and 1 mLmin^{-1} by a passive flow splitter to meet the EI ion source requirements. The comparison of spectra obtained in both conditions demonstrated that the signal intensity was enhanced at the higher flow rate. Adding water to ACN, 50/50 (v/v), resulted in a signal intensity decrease. All experiments repeated in acidified conditions by adding 1% FA to samples and solvents induced different fragmentations with adducts formations and a general reduction in signal intensity. UHPLC separation was carried out using a C18 column (50 x 2.1 mm, 1.8 µm) with water and ACN acidified with 1% FA in gradient mode at a flow rate of 0.2 mLmin^{-1}.

Chromatograms were acquired in NCI scan and selected ion monitoring modes.

Acknowledgment:
The authors are grateful to Agilent Technologies for providing the MS instrumentation.

MS-P5

COMBINATION OF TARGET AND UNTARGETED APPROACHES FOR UNRAVELLING WATER MICROPOLLUTANTS IN FISH FARMS AND WASTEWATERS

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Nowadays a huge number of pollutants and micropollutants are released in the aqueous environment by multiple routes and as a consequence the freshwater addressed to human consumption or food production as in the case of aquaculture may be contaminated with inorganic or organic contaminants. Taking into account the complexity of this actual matrices, the recent advances in analytical techniques and the high-resolution mass spectrometry (HRMS) provide the opportunity to detect a wide range of known and unknown contaminants by combining the suspect screening analysis (SSA) with non-target analysis (NTA) approaches. This work was conducted as part of the H2020-MSCA-RISE-2020 SusWater project with the aim to monitor the quality of different water matrices (such as wastewater and fish farms waters) and to tailor subsequently the proper restoration strategies aimed to water reuse. For this purpose, several samples were collected from aquaculture farms and municipal wastewater treatment plants (WWTP) located in Italy, Denmark and Spain. Two different solid phase extraction (SPE) protocols were employed to screen non-polar/moderately polar analytes and polar analytes and afterwards the obtained extracted samples were subjected to LC-HRMS applying SSA approach for the screening of 50 pesticides and 53 other widely diffused contaminants, and NTA approach exploiting the Full Scan data dependent acquisition mode. By means of GC-MS, it was also assessed concentration of odour substances, in particular geosmine and 2-methylisoborneol (MIB), lipophilic compounds formed as secondary by-products of bacteria.

Paracetamol was detected in all examined aquaculture plants and in particular several pharmaceutical residues were found in the plant located in Denmark at level of µg/L. In the inlet of WWTP of Turin, more significant content of drugs and pesticides was observed in respect to wastewater pilot plant in Spain.

MS-P6

HS-SPME AND GC-MS FOR VOLATILE COMPONENT ANALYSIS OF DRIED FRUIT WASTES

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Headspace solid phase microextraction (HS-SPME) technique coupled with gas chromatography and mass spectrometry (GC-MS) is the main technique used to extract, isolate and enrich the volatile fraction from the sample matrix[1]. HS-SPME is a simple, low-cost, solvent-free and sensitive technique for the analysis of volatile compounds with a wide boiling point range without any artefact[2]. However, the selection of the fibre and SPME extraction conditions can affect the sensitivity and accuracy of SPME analysis. HS-SPME is a technique that depends upon the equilibrium of experimental conditions, such as heating temperature, extraction time, sample volume, concentration of volatiles, and sample matrix. In this study, the volatile organic compounds (VOCs) profiles from grounded dried fruit wastes have been investigated and compared. The extraction of VOCs has been carried out by SPME fibres (CAR/PDMS, DVB/CAR/PDMS and PDMS/DVB) used at appropriate analytical conditions. Through a principal component analysis (PCA) and analyses of variance (ANOVAs), differences were highlighted. Identification of VOCs was performed by comparing MS data obtained with those of NIST library (match factor ≥ 80) and by calculating the experimental linear retention indices relative to a series of n-alkanes (C7-C30) the values were compared with the linear retention indices available in PubChem (https://pubchem.ncbi.nlm.nih.gov/), with a relative difference ≤ 2.5%. Furthermore, PubChem were used to describe the odour and flavour characteristics of identified VOCs. Differences in VOCs profile between the dried fruit wastes (pomegranate and prickly pear) and different parts (skin, pulp and seeds) were evaluated since there is an important relationship between the presence of volatile organic compounds in food and multisensory flavour perception and therefore the acceptability of a product[3].

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Acknowledgements:
This work was supported by the Apulia Region (Italy) through the programme “Aiuti ai programmi integrati promossi da MEDIE IMPRESE”, involving CIEMME Alimentari srl and the consulting of the University of Foggia.

MS-P7

DETERMINATION OF PESTICIDE RESIDUES IN HONEY USING HIGH RESOLUTION MASS SPECTROMETRY

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Honey can be contaminated with pesticides, in particular, neonicotinoids and pyrethroids, with potential risks for consumers health[1]. The simultaneous monitoring of pesticide residues represents an analytical challenge, in particular for a complex matrix as honey[1]. In this study, a simple and reliable methodology for the identification of 78 pesticides in honey samples was developed using the QuEChERS method, for the extraction and clean-up, followed by analysis with Ultra-high-performance liquid chromatography electrospray Q-Orbitrap mass spectrometry. Matrix effect can condition the analytical response and the method sensitivity[2], hence it was determined for each pesticide, in compliance with the Regulation (EU) 2021/8083. Firstly, the influence of injection volume and dilution factor on matrix effects were evaluated in order to choose suitable parameters, then the slopes of two different types of calibration curve, i.e. solvent-matched calibration (SMC) and matrix-matched calibration (MMC) were compared using the specific equation for matrix effect calculation[2,3]. A total of 78 pesticides belonging to the classes of neonicotinoids, organophosphorus, phosphorothioates, organochlorines, phenylpyrazoles and pyrethroids, were determined. An injection volume of 2 µL ensured good sensitivity, good peak shape and acceptable matrix effect[2]. SMC and MMC curves showed correlation coefficients ≥0.99. For more than 95% of residues the matrix effect resulted in insignificant (≤ ±20%) allowing the use of SMC curve for quantification according to SANTE/2020/12830. The developed method proved to be specific, sensitive, with limit of detection value of 0.503 to 12.0 $\mu g Kg^{-1}$ and limit of quantification value of 1.52 to 36.37 $\mu g Kg^{-1}$. Recovery results, evaluated at two spike levels of 10 and 50 $\mu g Kg^{-1}$, were between 85 and 110 %, with relative standard deviation ≤ 20%. This analytical method can be suitable to simplify routine control activities and further used to extend the application to other pesticide residues.

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Acknowledgements:
This work is supported by funding from the Ministero della Salute, Project code RC IZSPB 08/2020.

MS-P8

USING NITROGEN AND HYDROGEN AS ALTERNATIVE CARRIER GASES IN GAS CHROMATOGRAPHY COMBINED WITH FLAME IONIZATION DETECTOR AND MASS SPECTROMETRY.

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Currently, there is no intrinsic shortage of helium gas (alternative natural gas wells are being found with very high helium amounts[1]), but the price of raw material will increase in the next years[1]. Thus, if and when the helium supply is disrupted, and the need to reduce the cost per analysis has led to investigations of hydrogen (H_2) or nitrogen (N_2) as alternative carrier gases for gas chromatography (GC) analysis combined with flame ionization detection (FID) and mass spectrometry (MS). Even though H_2 gas has excellent chromatographic separation efficiency with the widest range of useful linear velocities when compared to other carrier gases, important precautions must be taken because of safety concerns. On the other hand, N_2 is also considered a valid and sustainable alternative due to its inertness, readily available (can be generate *in-situ* using a generator), low expensive, and safe.

The purpose of this research is to explore the performance of N_2 and H_2 as alternative carrier gases in GC analyses using the most common detectors such as FID at atmospheric pressure, and MS under vacuum conditions. Finally, particular attention was dedicated to the separation of terpenes and oxygenated derivatives in *Citrus* essential oils.

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MS-P9

PUSHING PFAS POSSIBILITIES: THE HUNT FOR ULTRA SENSITIVITY TO REACH PPQ EPA HEALTH ADVISORY LEVELS

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Per- and polyfluoroalkyl substances (PFAS) are man-made chemicals used as surfactants in chemical processes and have been used in industry and consumer products since the 1940s. PFAS are characterized by a chain of strong fluorine-carbon bonds, leading to an incredibly stable chemical. This stability prevents PFAS from breaking down easily and means they are extremely persistent in our bodies and the environment, leading PFAS to sometimes being called “forever chemicals”. Since 2008 Waters has been pioneering PFAS analysis, providing turnkey applications for complete analysis solutions from standards and reagents to columns and LC-MS systems. This work focused on reaching the more stringent limits of the EPA HALs, detailing a PFAS analytical workflow approach using SPE extraction with Oasis™ WAX forPFAS Cartridge to enrich water samples with analysis performed on a Waters™ ACQUITY™ Premier UPLC™ System and Xevo™ TQ Absolute MS with data analysis using waters_connect™ for Quantitation software.

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MS-P10

REAL-TIME MONITORING OF COMPOUND MIGRATION FROM FOOD CONTACT MATERIALS: A PILOT STUDY USING CP-MIMS-MS/MS

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The migration of hazardous chemicals from food contact materials (FCMs) is a real concern to human health[1]. Bisphenol A (BPA), widely used for the production of polycarbonate plastics and epoxy resin used as FCMs, exhibits toxic, endocrine, mutagenic and carcinogenic effect. In 2022 the European Food Safety Authority has re-evaluated the risks to public health from the presence of BPA in food and proposed to considerably lower the tolerable daily intake from 4 µg/kg to 0.2 ng/kg bw/day[2].

In this context, the development of innovative analytical methods plays a key role to evaluate the conformity and safety of FCMs. Condensed Phase-Membrane Introduction Mass Spectrometry (CP-MIMS) is an innovative technique that utilizes semipermeable PDMS membrane interfaces to perform real-time dynamic analysis[3]: compounds that permeate through the membrane are collected by a condensed acceptor phase and directly transferred to a mass spectrometer. As a part of a program of a research project devoted to the development of advanced methods for food safety, a pilot study was performed to evaluate the potential of CP-MIMS for the real-time measurement of BPA migration from FCMs into food simulants. A syringe pump was used to deliver a mixture of methanol-heptane acceptor phase through the lumen of PDMS hollow fiber membrane probe exposed to the aqueous sample and entrained into the electrospray ionization source. The permeated BPA was analyzed by the LTQ XL linear ion trap mass spectrometer in MS/MS acquisition mode. Preliminary results showed a good permeation of BPA at ng/mL level with a signal rise time lower than 1 min. To get knowledge about BPA permeation and to find the optimal experimental conditions, a full factorial design of experiments was performed examining the effects of stirring velocity and sample pH. Further analysis will include a real-time investigation of BPA migration into food simulants from commercial plastic FCMs.

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Acknowledgements:

Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 341 of 15/03/2022 of Italian Ministry of University and Research funded by the European Union – NextGenerationEU Award Number: Project code PE0000003, Concession Decree No. 1550 of 11/10/2022 adopted by the Italian Ministry of University and Research, CUP D93C22000890001, Project title "Research and innovation network on food and nutrition Sustainability, Safety and Security – Working ON Foods" (ONFOODS).

Poster Elettroanalitica

HOW THE ELECTRODEPOSITION CONDITIONS OF PALLADIUM AFFECT HYDROGEN ABSORPTION: AN X-RAY DIFFRACTION EVALUATION

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Palladium electrodeposition has been used for many years in the electroplating industry because of the technical and aesthetic properties that this metal offers. Its use for decorative applications has become widespread since the 1980s as a substitution for nickel and it is now used both as a final coating and as an intermediate layer to improve corrosion resistance, increase the adhesion of subsequent precious deposits and act as a diffusion barrier layer.

The main restriction of all palladium and palladium alloy electroplating baths is the tendency to form deposits characterized by the presence of microcracks due to the evolution of large quantities of hydrogen during the metal reduction and its consequent co-deposition. In fact, palladium is able not only to absorb hydrogen in atomic form but also to dissolve it to form two bulk hydride phases known as α-PdH$_x$ ($x \sim 0.02$) and β-PdH$_x$ ($x \sim 0.67$) which have long been studied and investigated for many different applications[1]. The preferential deposition of either phase depends on the conditions of temperature, current density, etc. that occur during electrodeposition, which generally promote the formation of the β-PdH$_x$ phase. Microfractures result from hydrogen desorption associated with the lattice contraction that occurs in the transition from the β-PdH$_x$ to the thermodynamically stable α-PdH$_x$ phase[2]. In this latter phase, the face-centered cubic lattice of Pd is not changed and any further desorption of hydrogen does not cause factures. The aim of this work is to evaluated the performance of a new palladium bath by fabricating samples under different conditions and performing the depositions under both direct and pulsed currents. The use of pulsed current is beginning to gain popularity in the electrodeposition of metals and alloys because of the advantages it can offer in terms of deposit quality, decreased organic content, and lower metal consumption. The samples were analyzed by X-ray diffraction technique that makes it easy to distinguish the two hydride phases due to the presence of a diagnostic peak at 39° and 40° of the beta and alpha phases, respectively[3].

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Acknowledgements:

The authors acknowledge for the support offered by Fondazione CR Firenze, Fondazione per la Ricerca e l'Innovazione dell'Università degli Studi di Firenze and Confindustria Firenze within the FABER4 project.

EL-P2

MORPHOLOGICAL AND SPECTROSCOPIC CHARACTERIZATION OF SELF-TEMPLATED HIGLY POROUS GOLD (h-PG) FOR ENZYME-BASED AMPEROMETRIC BIOSENSORS

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In the last decades, nanomaterials have shown great advantages in terms of functional properties for a wide range of technological applications [1]. Metal nanoparticles provide a lot of advantages compared to macroelectrodes, such as enhancement of mass transport, catalysis, high effective surface area and control on the electrode conductive microenvironment. Highly porous gold (h-PG) can be synthesized by using a chemical approach and electrodeposition. The main advantages of the electrodeposition method are the thickness, roughness and size control of the h-PG layer [2].

In this work h-PG was directly electrodeposited onto a gold electrode (AuE) by using a two-steps method: 1) sweeping the potential in a 10 mM HAuCl4 solution (supporting electrolyte 2.5 M NH4Cl); 2) applying a potential -3 V vs. Ag|AgClsat [3,4]. Afterwards, the nanostructured electrodes were characterized by scanning electron microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). The so modified electrodes were further characterized with $Fe(CN)6^{3-/4-}$ by cyclic voltammetry and electrochemical impedance spectroscopy, and compared to the naked gold electrode (AuE) in order to determine the electroactive area (AEA), electron transfer rate constant (k0), real surface area (Areal) and the roughness factor (ρ) [5]. Finally, the electrodes were modified with FDH and poly(vinyl alcohol), N-methyl-4(4'-formylstyryl)pyridinium methosulfate acetal (PVA-SbQ) to detect D-(-)-fructose in fruit juice samples as potential on-line biosensor for food industrial production processes [6].

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EL-P3

VOLUMETRIC POWER OUTPUT OF GLUCOSE/O_2 FULLY PRINTED ENZYME-BASED BIOFUEL CELL

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Enzymatic fuel cells (EFCs) have been proposed to catalyze oxidation of fuels at anodes and/or reduction of oxidants at cathodes and provide electrical power. EFCs can be divided into two main groups: 1) mediated electron transfer (MET) devices, in which redox species are used to transport the electrons between enzyme and electrode surface; 2) direct electron transfer (DET) based biodevices, where the enzyme is able to communicate directly with the electrode[1]. Moreover, there are some issues in defining the power output, especially considering anodes and cathodes with different sizes. For example, a H_2/O_2 EFC combines a 6 cm^2 bilirubin oxidase-modified cathode with a 1.2 cm^2 hydrogenase-modified anode to balance the catalytic performance as a function of the H_2-air mixture used[2]. The raw power output must surely now be reported in all cases? It now seems valuable to define the volumetric power of bioelectrodes in mW/cm^{-3} [3].

The aim of this work is to study the influence of electrode size on the performance of glucose/O_2 enzymatic fuel cell (EFC). The proposed EFC will encompass an efficient MET bioanode, employing glucose oxidase (GOx) modified graphite printed electrode (all materials will be enclosed in a newly formulated ink), and a DET biocathode, consisting of bilirubine oxidase (BOD) modified graphite printed electrode[4,5]. The EFCs will be assembled symmetrically and asimmetrically using three different electrode sizes: (a) 0.1 cm^2, (b) 1 cm^2 and (c) 10 cm^2. All Power output will be normalized by the EFC volumes instead of the electrode areas. Finally, the EFCs were tested in human serum and saliva to explore their Limit of Detection (LOD) and their potential application as self-powered glucose biosensor integrated in wearable devices.

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EL-P4

CATECHOL-BASED LIGANDS FOR IRON SPECIATION IN SEAWATER: STABILITY AND ELECTROCHEMICAL ANALYSIS

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Iron speciation in seawater is an aspect of fundamental relevance in oceanographic studies as iron plays a key role in regulating the primary productivity of ocean systems. In fact, the amount of iron in seawater is a limiting factor for the growth of phytoplankton, even in the presence of large quantities of macronutrients. The presence of iron is accordingly linked to the CO_2 cycle and its absorption phenomena by marine organisms[1].

Competitive Ligand Equilibration – Cathodic Stripping Voltammetry (CLE-CSV) is the method of choice for the study of iron bioavailability, combining selectivity for different iron species and high sensitivity for ultratrace determination. A previous CLE-CSV method proposed by Sanvito et al.[2] uses 2,3-dihyroxynaphthalene as an iron ligand: however, it undergoes a relatively slow oxidation at the alkaline pH values typical of seawater. To overcome this issue, various catechol-based species, substituted with electron-attracting groups, have been tested aiming at limiting its oxidation kinetics[3]. The following molecules were evaluated: 4,5-dichlorocatechol (DCC), tetrachlorocatechol (TCC), 2,3-dihydroxybenzoic acid (2,3-DHBA), 3,4-dihydroxybenzoic acid (3,4-DHBA), 4,5-dihydroxy-1,3-benzenedisulfonic acid (SULF).

The degradation kinetics was studied in ultrapure water at pH 8.2 by NMR spectroscopy: as a result, all the binders are stable for at least 24 hours under the employed experimental conditions. The analytical performances of the ligands were subsequently determined by systematic measurements of the sensitivity in UV treated seawater and satisfactory results were achieved, except for SULF whose iron complex was not electroactive.

DCC provided the most suitable for the developing of a CLE-CSV procedure: the electrochemical parameters of the DCC-iron complex were measured to obtain a more in-depth knowledge of the proposed method. Moreover, the sensitivity and reproducibility of the voltammetric signal were optimized by systematic investigation of the chemical (pH, ligand concentration) and electrochemical parameters (voltage step, square wave frequency and amplitude, deposition time).

As a results, DCC has been shown to have suitable electrochemical and stability characteristics for the study of iron speciation in seawater.

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We would like to thank Professor Angelo Maspero for his technical support in NMR measurement.

EL-P5

STUDY OF ELECTROCHEMICAL SENSORS BASED ON MULTI-WALLED CARBON NANOTUBES (MWCNTs) AND BT$_2$T$_4$ OLIGOMERS FOR ENANTIOMERIC DISCRIMINATION.

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Enantiomer discrimination plays a crucial role in electroanalytical chemistry because chiral molecules' enantiomers share similar physicochemical characteristics and electrochemical behaviour, except in chiral environments where diastereomeric situations arise due to energy differences. This discrepancy leads to vary energy levels between diastereomeric states. Hence, enantioselective electrochemistry involves electron transfer processes under asymmetric or dissymmetric conditions, such as on a chiral electrode surface or in a chiral medium[1]. Chiral electrochemical sensors employ different approaches[2], but the most notable strategy involves "inherently chiral" molecules[3] as both electrode surfaces[4] and media[5]. One commonly used inherently chiral molecule is the oligo-2,2'-bis(2,2'-bithiophen-5-yl)-3,3'-bi1-benzothiophene monomer known as BT$_2$T$_4$. Studies[6] have demonstrated that when these thiophene structures are deposited on an electrode surface, they can effectively discriminate and quantify enantiomers of chiral probes. In this study, we report, for the first time, the modification of a glassy carbon electrode (GCE) with Multi-Walled Carbon Nanotubes (MWCNTs) and the inherently chiral oligo-BT$_2$T$_4$ film. This modification aimed to leverage the advantages of both materials (enhanced electrochemical signal provided by MWCNTs and the enantiodiscrimination capabilities of oligo-BT$_2$T$_4$). Furthermore, this chiral surface demonstrated successful enantioselective detection of chiral molecules, exhibiting favourable sensitivity and selectivity towards the enantiomers of the target compound, but also excellent stability and reproducibility.

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EL-P6

FUNCTIONAL PROPERTIES OF HYDROGEN PERMEATION BARRIERS ON STEEL

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In the battle to reduce emissions globally, hydrogen is one of the possible solutions as energy carrier. Production, storage and transportation of hydrogen are challenges both for fundamental and applied research. This presentation focuses on the type, properties and production of hydrogen permeation barriers on steels applied to prevent or at least reduce hydrogen ingress into steel and avoid hydrogen embrittlement. In this context the results of a review of hydrogen permeation barriers (HPB) on steel and stainless steels are presented and commented. HPB can be applied by a variety of methods, including vapor deposition techniques (PVD, CVD), sol-gel and electrochemical deposition. Hydrogen Permeation Barriers (HPB) should have few defects such as pores, cracks and should exhibit a compact microstructure, low hydrogen diffusion coefficient, low hydrogen permeability and high Permeation Reduction Factor (PRF). Steel substrates and selected HPB coatings will be characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM/EDX), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence spectroscopy (XRF) and mechanical tests. The system coating/substrate will be investigated with electrochemical permeation tests using the Stachurski cell [1]. Preliminary results of XPS, XRD, SEM analysis of X60 pipe steel substrate and HPB coatings will be presented together with electrochemical permeation tests.

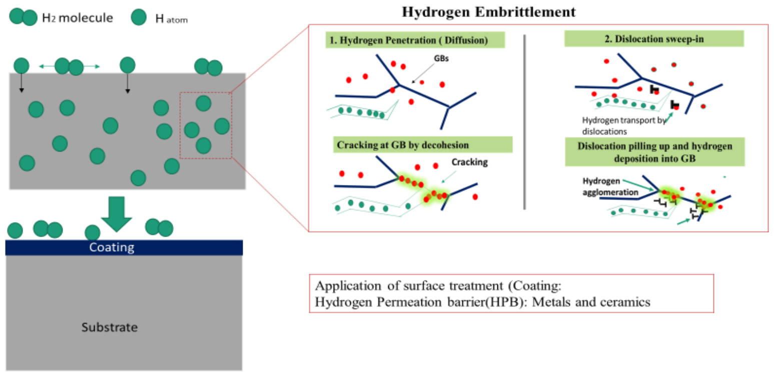

Figure1: (from left - clockwise) scheme of hydrogen permeation on steel; scheme of hydrogen embrittlement [2].; hydrogen permeation-barrier: metal, oxides and ceramics deposited on steel surface.

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Acknowledgements: PNNR (CUP F22B22000560005 - BORSE PNRR DM 352) and Rina Consulting CSM S.p.A (CUP F22B22000560005 – Cof. RINA Consulting - CSM S.p.A.) are thanked for co-funding this project. The financial support of the European Union NextGenerationEU under the National Recovery and Resilience Plan (NRRP) of Ministero dell’Università e della Ricerca (MUR) (Project code PE0000021, “Network 4 Energy Sustainable Transition, NEST) is acknow.

EL-P7

COULOMETRICALLY DETERMINED ANTIOXIDANT CAPACITY (CDAC): METHOD OUTLINE

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A plurality of methods for the determination of the antioxidant capacity of different samples (foods, plasma, etc.) have been proposed, and it is well established that there is no correlation between any one of the parameters determined *in vitro* and the true antioxidant capacity *in vivo*. Each of the methods proposed up to now gives a different indication, so rather than an absolute antioxidant capacity, it can be useful to compare the antioxidant capacity of different samples or of how it changes with time in a single sample[1]. In our laboratories, an already known electrochemical method, originally developed for the determination of the number of double bonds in hydrocarbons, the so-called Bromine Index[2], has been slightly modified, and used to determine a Coulometrically Determined Antioxidant Capacity (CDAC) of a wide variety of samples [3-4]. Typically, to determine its CDAC value a sample is oxidized at the anode of an electrochemical cell. The electrons involved in the redox reactions which take place at the anode are measured. The higher the antioxidant capacity of the sample, the more electrons are involved in the process. With the proposed method, micro amounts of reducing species can be determined whit a high accuracy. It is proposed to introduce for each kind of sample an index, *R*, which indicates the ratio between the $(CDAC)_x$ of a sample x, and the $(CDAC)_{STD}$ of a standard reducing molecule, specific for the chosen sample.

$$R = \frac{(CDAC)_x}{(CDAC)_{STD}} \qquad (1$$

Coulometric analysis offers advantages such as high sensitivity (traces antioxidants), easy sample preparation, fast response time, the possibility to directly measure the antioxidant capacity without the need for additional chemical reactions; furthermore, it can be used for different types of samples, analyzed as is or diluted in water or water-organic phases. The CDAC provides a reliable and efficient method for assessing the antioxidant properties of substances, contributing to the understanding of their potential health effects, and aiding in the development of new antioxidant-rich products.

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Poster

Equilibri

PyES, AN OPEN-SOURCE SOFTWARE FOR THE COMPUTATION OF IN SOLUTION AND PRECITATION EQUILIBRIA

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From a survey conducted inside the Network for Equilibria and Chemical Thermodynamics Advanced Research (COST ACTION – NECTAR CA18202)[1] emerged the need for new and improved computer tools for the study of thermodynamic equilibria. For this reason, we decided to write PyES: a new, open-source, practical, modern, and multi-platform Python application, based on the principles of ES4, a computer program written by Prof. Silvio Sammartano from the Università degli Studi di Messina, and his co-workers, in BASIC language[2].

PyES has two work modes: potentiometric titration simulation and species distribution at different concentration of one of the components present. Direct improvements from ES4 are the ability to manage solid species and to perform calculations at variable ionic strength, considering the dependence of the stability constants on it by an expanded Debye-Hückel equation. Moreover, it can boast a new and improved graphical interface, allowing easier access to the system definition and results export. New improvements in this last version (v1.0.0) include the computation of uncertainties for the calculated concentrations, improved precipitate calculation, new quick interface commands, and general bug fixes. An article in open-access form is available for consultation[3] and the software can be downloaded for all major platforms at the link: https://github.com/Kastakin/PyES.

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This publication 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, www.cost.eu, https://cost-nectar.eu/).

SEQUESTERING ABILITY OF SODIUM ALENDRONATE TOWARDS CALCIUM AND MAGNESIUM IN NACL AQUEOUS SOLUTIONS

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Bisphosphonates (BPs) are a class of compounds that have therapeutic activities for the treatment of bone diseases such as osteoporosis, Paget's disease, and hypercalcemia. The presence of P-C-P bond gives the molecules low toxicity, high thermostability and resistance to enzymatic degradation. Generally, BPs have a high ability to bind metal ions due to the mobility and flexibility of the neighboring functions of the phosphonates. In this work, a second-generation bisphosphonate, Alendronate (ALN^{4-}) (or sodium [4-amino-1-hydroxy-1-(hydroxy-oxido-phosphoryl)-butyl]phosphonic), was examined to evaluate its acid-base properties and ability to interact with cations of biological importance, as calcium and magnesium. A thorough literature survey revealed that many coordination studies have been carried out to determine metal chelating abilities of clinically used bisphosphonates, but coordination studies of ALN^{4-} with Ca^{2+} and Mg^{2+} are quite confused. The first step of experimental investigations was to determine by potentiometry, the protonation constants of ALN^{4-} in NaCl(aq), and $(C_2H_5)_4NI$(aq) at different ionic strengths and temperatures ($283.15 \leq T/K \leq 318.15$). The protonation constants determined in NaCl(aq) resulted lower than those obtained in the tetraalkylammonium salt. The medium effect was interpreted both in terms of variation of the activity coefficients with ionic strength (Debye–Hückel type and SIT), and in terms of formation of weak complexes between ALN^{4-} and the ions of the supporting electrolytes.

From the investigations on the interactions with Ca^{2+} and Mg^{2+}, carried out in NaCl aqueous solutions at different ionic strengths and at $T = 298.15$ K, resulted that in each case, the speciation model is featured by the MLH_3, MLH_2, MLH, ML species, even if in specific condition, the formation of other minor species is possible.

The sequestering ability of ALN^{4-} towards the metal cations was evaluated computing the $pL_{0.5}$ parameter at different pH and ionic strength values. Results reported in this work may be helpful in the assessment of the use of alendronate as effective chelating agent and for better understanding the mechanism of action of this molecule as a drug.

Eq-P3

EQUILIBRIUM STUDIES ON A PESTICIDE METABOLITE, THE AMPA, AND ON THE DIMETHYLTIN(IV) CATION IN MULTICOMPONENT SYSTEMS

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Glyphosate is widely used as herbicide, controlling the broadleaf weeds and grasses; it gives different degradation products and the main of them is the aminomethylphosphonic acid[1], AMPA. The purpose of this study is to broaden the equilibria knowledge, in terms of the acid base properties of AMPA and dimethyltin(IV), DMT, in multicomponent solutions that simulate the composition and behaviour of natural waters as the seawater, and a biological fluid like the human plasma. The protonation and the hydrolytic constants of AMPA and DMT, respectively, have been determined by potentiometric titrations, in synthetic seawater at different salinities ($15 \leq S \leq 45$) and temperatures ($288.15 \leq T/\mathrm{K} \leq 313.15$), while in simulated plasma at average ionic strength $\bar{I} = 0.2$ mol dm^{-3} and at the physiologic temperature $T = 310.15\mathrm{K}$. At these experimental conditions, the complexing ability of AMPA towards DMT has been tested and the speciation models determined. The experimental data obtained at the different conditions of I and T have been modelled by using a Debye-Hückel type and the Van't Hoff equations. In a previous study on this metabolite[2] its capacity to form complex species with some metal cations: Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+} and Al^{3+}, has been reported in aqueous solutions of NaCl, the major inorganic component of the natural waters[3]. The sequestering ability of AMPA towards the DMT and the metal cations already investigated[2] has been compared by means the empirical parameter $pL_{0.5}$[4].

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Eq-P4

BINDING PROPERTIES OF SERUM ALBUMIN TOWARDS SULFONPHTHALEIN DYES: EXPLORING THE ROLE OF THE DIFFERENT SPECIES IN SOLUTION

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The interaction of serum albumins with cost-effective and commercial dyes, such as Bromocresol Green, BCG, have attracted great interest among scientists searching for simple and efficient detection methods for laboratory practices and commercial assays[1]. Indeed, the proper use of sulfonphthalein dyes enables the easy quantification of serum proteins by employing common spectrophotometric or colorimetric techniques. Several studies dealt with the characterization of the binding features of serum albumins with suitable dyes for detection purposes[2] but most of them were conducted at non-homogeneous conditions (different pH values, ionic strength, buffer, medium composition) thus precluding a rational and complete picture of the dye recognition ability. Within this framework, we decided to carry out a systematic solution equilibria study to examine the binding properties of bovine serum albumin (BSA) towards selected halogen-containing sulfonephthalein dyes (Figure 1) having similar structures but different acid-base properties (pK_a values range from 4.42 to 6.72)[3]. UV-Vis titrations of BSA into the dye (buffered) aqueous solutions at different pH values and controlled ionic strength allowed us to determine the conditional stability constants of the protein-dye adducts as well as to unveil the role of the different proton species of the sensing agents on the recognition process of BSA in solution.

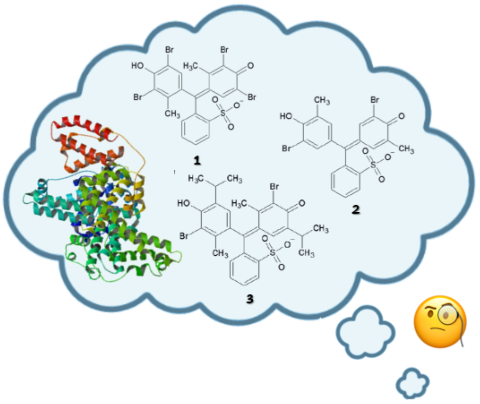

Figure 1: Structures of the investigated dyes, Bromocresol Green (1), Bromocresol Purple (2) and Bromothymol Blue (3).

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HOW RELIABLE IS THE VALUE OF A BINDING CONSTANT? THE Ag(I)-ANTHRACENYL BISCARBENE/DNA SYSTEM

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How to efficiently and robustly find the value of a binding constant between a small molecule and a nucleic acid? The connected calculations appear in many papers as some easy routine. Instead, the procedure to extract numbers from experiments deserves many tricky aspects, which may turn our values random[1].

In this contribution, we have studied the binding of a nucleic acid-intercalator ($[Ag(BIA)_2]^+$, Figure 1) to natural DNA from the calf thymus (CT-DNA, B type). We did spectrophotometric and spectrofluorometric titrations under different salt content conditions. They were analysed using one-wavelength equations or multi-wavelength software (HypSpec®) to extract binding constants data. We will comment on the numbers obtained, their dispersion, and how the latter influences the discussion of salt dependence in the frame of the Record's theory[2].

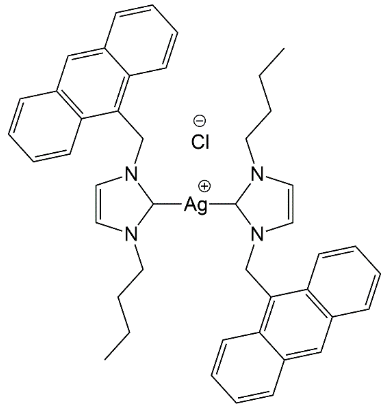

Figure 1: Molecular structure of bis(1-(anthracen-9-ylmethyl)-3- butylimidazol-2-ylidene) silver chloride, $[Ag(BIA)_2]Cl$

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Acknowledgements:

We thank CIRCMSB (Consorzio Inter-Universitario di Ricerca in Chimica dei Metalli nei Sistemi Biologici). This contribution is part of the work from COST Action CA18202, NECTAR Network for Equilibria and Chemical Thermodynamics Advanced Research, supported by COST (European Cooperation in Science and Technology).

Eq-P6

ADSORPTION OF Cd (II) IONS FROM AQUEOUS SOLUTIONS ONTO BIOCHAR FROM BIOMASS WASTE

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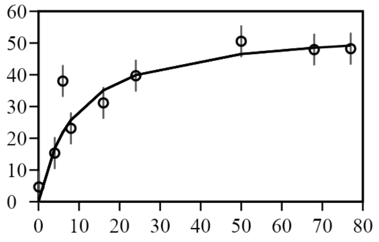
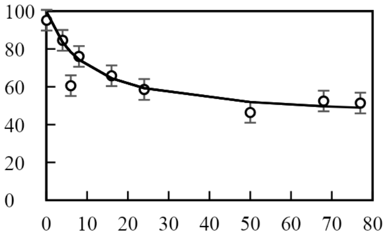
Biochar is a carbon−based material obtained by pyrolysis (in Argon atmosphere) of biomass such as manure produced by cattle farms. The use of biochar in agricultural soils improves the properties of the soil and the yield of agricultural products. Effects of biochar and biochar−compost mixtures on soils favor plant growth and induce an immobilization of heavy metals and organic pollutants. In the present work, the adsorption of Cd(II) ions onto biochar at 25 °C in 0.1 M $NaClO_4$ as ionic media has been studied. Preliminary to adsorption study has been the determination of protolysis constants conducted by potentiometric methods by using of glass electrode. The potentiometric data processed by numerical methods[1] agree that the surface of solid presents acid sites and basic sites, with the following protolysis constants:

$$>ROH + H^+ \leftrightarrows >ROH_2^+ \qquad \log K_R = 2.6 \pm 0.1$$

$$>TOH \leftrightarrows >TO^- + H^+ \qquad \log K_T = -8.5 \pm 0.1$$

The adsorption of Cd(II) ions from aqueous solutions has been conducted by isotherm and kinetic studies. The isotherm data collected follow the Langmuir model with a maximum capacity: $\Gamma_0 = (95 \pm 2)$ mg/g as well as with an adsorption constant: $K_L = (0.10 \pm 0.06)$ dm^3/mmol. In addiction the adsorption process of the Cd(II) ions reaches equilibrium after about 24 hours (Figure 1). The kinetic data are compatible with a pseudo−second order model, where the intraparticle diffusion represents the slow stage of the process. The measurements carried out in aqueous solutions show that the use of biochar prepared from solid livestock waste allows to obtain a removal by adsorption of 50% of the Cd (II) ions at pH = 5.5 (Figure 2).





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Poster

Alimenti

ALI-P1

QUALI-QUANTITATIVE CHARACTERIZATION AND VALORIZATION OF SOLID AND LIQUID WASTES FROM EVO AGRIFOOD CHAIN

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Nowadays one of the main topics in industrial field is the possibility to reduce waste products and recycling components, materials and energy. This circular bioeconomy approach is particulary suitable with olive milling industry, that often generated large amounts of solid and liquid residues[1]. However, a high concentration of active compounds was often observed in these wastes (such as phenols, polyphenols, proteins, fats, tannits etc.) with potential applications in cosmetics, pharmaceuticals and supplemental food[2,3].

On this basis, the aim of our work has been to assess the presence of polyphenols, and the quantification of them both in dried olive pomace and in vegetative water obtained using two-phase and a half and three-phase decanter. A simple ultrasound-assisted solid-liquid extraction (UA-SLE) has allowed to obtain a good recovery of the analytes, minimizing the matrix effect and to use of only water and ethanol mixtures, avoiding the presence of toxic solvents.

After the sample preparation, the analyses was conducted using high-performance liquid chromatography (HPLC) with diode array detector (DAD), with reverse phase C18 column, a well-known instrumentation and certainly more affordable than other as liquid-chromatography coupled mass spectrometry. The confirmed presence of these analytes, that have antioxidant, antimicrobial and anti-inflammatory activity, allows to implement the recovery of these waste products, which can be processed and converted into products having these effects, without excluding the possibility of investigating further important application properties.

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CHEMICAL PROFILING AND ANTI-INFLAMMATORY/ANTI-LIPOGENIC ACTIVITY OF AN ARTICHOKE STEM EXTRACT

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Artichoke (*Cynara cardunculus*) extracts have long been recognized to exhibit numerous health benefits, mostly attributed to phenolic compounds[1]. Among these, esters of caffeic acid and (−)-quinic acid play a key role, which are particularly abundant in the stems[1]. Accordingly, this part of the vegetable was selected for the present study. The phenolic mixture was extracted through a maceration protocol from freeze-dried artichoke (var. Violetto) stem powder. A water/methanol (20:80, v/v) solution was used as extraction solvent. After centrifugation and filtration of the green coloured supernatant, the extract was evaporated until dryness. Subsequently, the extract was reconstituted in water and submitted to a SPE-based extraction process using C18 cartridges. By this way, flavonoids were removed from the initial extract, and the new extract then analyzed with an optimized HPLC method. The chromatographic analysis was carried out under RP conditions with a linear gradient of methanol in water (plus formic acid), revealed high concentrations of 5-caffeoylquinic acid (chlorogenic acid, 5-CQA) and 1,3-dicaffeoylquinic acid (Cynarine). A deeper insight into the chemical composition of the extract was made possible by UHPLC-MS/MS analysis with a Q-ToF detector, which revealed the presence of minor amounts of other chlorogenic acid isomers. After excluding the cytotoxicity of the purified artichoke stems extract on Caco2 and HepaRG cell lines in a wide concentration range, the fully characterized sample was evaluated *in vitro* in terms of cytoprotective activity on non-tumor liver cells inflamed with LPS or treated with 1% ethanol (v/v) and/or fatty acids to mimic a condition of fatty liver[2,3]. The extract was found to reduce the expression of inflammatory cytokines secreted by LPS-treated cells and to increase cell viability in this model. Moreover, the extract reduced the number of lipid droplets in HepaRG treated with free fatty acids and/or ethanol increasing cell viability. Our findings suggest that this extract from artichoke stems has a promising anti-inflammatory and anti-lipogenic effects like 5-CQA in *in vitro* steatosis model.

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ALI-P3

DETERMINATION OF 289 PESTICIDES IN ITALIAN EGGS FROM LARGE RETAIL: ORGANIC *vs* CONVENTIONAL PRODUCTION

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The global population is predicted to grow to 9.7 billion by 2050, representing an increase of about one-third compared to 2015. Food security is a current concern and a healthy and sustainable global diet is strongly recommended.

In the worldwide dietary, eggs, frequently consumed thanks to affordable market prices, occupy a key position as food of high nutritional value. In this context, the European Union (EU) has shown an upward trend in egg consumption, besides the fact that commercially EU is one of the world's largest poultry meat and eggs producers. Furthermore, animal welfare and food safety are key topics, thus solid European legislative frameworks have been implemented.

Although conventional production systems have seen the highest increase over the last decade, however the demand for organically produced eggs has been experiencing a growth nowadays, due to the consumer perception that organic products have more benefits on sustainability, animal welfare and health.

However, since differences in chemical contamination from conventional to organic production can occur due to different rearing systems[1], relevant pesticides including the ones ranked as persistent organic pollutants (POPs), should be investigated.

In the context of Food Safety and Zero Pollution action plan, the EU has established action strategies for health consumer protection, reducing, at once, environmental pollution of ecosystems. Regarding pesticides, Multiannual Control Programmes are run within EU to ensure compliance with MRLs and assess the consumer exposure to pesticide residues in food of plant and animal origin.

In this perspective, the scope of this work was to compare the pesticide environmental contamination of Italian eggs produced by organic and conventional systems. Thus, in the biennium 2018-2020, 112 Italian egg samples (58 and 54 belonging to organic and enriched cages rearing systems respectively) have been collected in different Italian large retailer points. All samples were analysed for determining a total of 289 pesticides with a QuEChERS-based multiresidue analytical method and instrumental analysis by means of UHPLC-HRMS and GC-MS/MS. The method was previously validated and accredited following SANTE/2017/11813 and ISO IEC 17025:2017 respectively.

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Project financed by Italian Ministry of Health (MSRCTE09/16).

ALI-P4

UNTARGETED VOLATOLOMICS BY HEADSPACE MICROEXTRACTION GAS CHROMATOGRAPHY-MASS SPECTROMETRY (HS-SPME-GC-MS) FOR THE IDENTIFICATION OF QUALITY MOLECULAR MARKERS IN FRESH-CUT ICEBERG LETTUCE

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Fresh-cut iceberg lettuce is an appreciated product by consumers for its nutritive properties, convenience, and ease of use[1]. This product has a natural waxy and edible coating which naturally protects the product from external exposures. However, in the case of freshly cut vegetables, these coatings are damaged, and the surface of the product is exposed to chemical or microbial factors[2]. Indeed, the problem associated with ready-to-use vegetables is their short shelf-life (5–7 days for iceberg lettuce, stored at 4°C). Approximately on the seventh day of storage, these products suffer from loss of freshness, aroma, and quality. To extend their shelf life, they are often stored in modified atmosphere packaging (MAP)[3]. The study of the aromatic profile of these products can give useful information about their quality during the storage time: in fact, some of these volatile compounds are naturally released by horticultural products, but others are produced only during vegetable cutting or from stress-induced metabolic pathways triggered by minimal processing, becoming potential biomarkers of quality changes[4].

In this study, the influence of two storage modalities, passive (air) MAP and active MAP (< 5% O_2), on sensory quality parameters and the development of volatile organic compounds (VOCs) at different storage days were evaluated. An untargeted volatolomic approach by headspace solid-phase microextraction (HS-SPME) followed by gas chromatography-mass spectrometry (GC–MS) is described[5]. More than 400 volatile compounds were found in the lettuce samples and within the class of all the identified aromatic compounds, the most significant VOCs, accurately chosen considering their behavior in function of the storage time, were selected for a semi-quantitative evaluation using the peak area values. Compounds that could represent quality molecular markers were identified by multivariate data analysis (Principal Component Analyses and Partial Least Squares regression), in correlation with the type of MAP applied during the product storage. Finally, two volatile compounds (ethyl alcohol and acetaldehyde, for active and passive MAP, respectively) have been proposed as suitable markers to assess the quality of the product and the shelf-life of fresh-cut iceberg lettuce.

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ALI-P5

CHARACTERIZATION OF VOLATILE COMPOUNDS IN ITALIAN CIDER USING GC×GC-MS AND MULTIVARIATE ANALYSIS

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Cider is a traditional alcoholic beverage obtained by partial or complete fermentation of juice (fresh or reconstituted), with or without the addition of sugar, water or flavouring[1]. In recent years, a global increase in its consumption has been recorded: this popularity may be related to the specific organoleptic profiles of ciders, which are closely associated with the variable contents of many aromatic compounds in the final beverage[2]. One such group is commonly known as 'volatile organic compounds' (VOCs). Aroma profile, the utmost criteria in assessment of cider quality, is composed by many VOCs belonging to different chemical families[3]. Gas chromatography (GC) coupled with different detectors, such as mass spectrometry (MS) and flame ionization (FID) is the current technique for the robust analysis of VOCs. The complexity of most food matrices requires the isolation of the analytes as precursors before their introduction into the chromatographic system[4]. In this context, solid phase microextraction (SPME) offers considerable advantages. What is still not widely used in the characterization of VOCs in cider is the comprehensive two-dimensional gas chromatography[5,6]. The aim of this work is the characterization of different Italian ciders by HS-SPME-GC×GC-ToFMS. Multivariate statistical approaches play a crucial role, allowing to extrapolate meaningful information from the data. After building the clean dataset of the analysed VOCs, three other datasets were obtained, normalized respect to the three internal standards used (Acenaphthene-d_{10}, 1,4-Dichlorobenzene-d_4, Naphthalene-d_8), to evaluate their influence on the analytical method. These datasets have been analysed with main unsupervised methods of Machine Learning, Principal Component Analysis (PCA), Cluster Analysis (CA) and t-distributed Stochastic Neighbor Embedding (t-SNE), which made it possible to highlight the robustness of the method, showing similar results for the different datasets. Moreover, the exploratory analysis allows to identify different classes of ciders, which are distinguished by the fermentation process or the addition of flavouring, such as hops.

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ALI-P6

HS-SPME/GC–MS AND CHEMOMETRIC APPROACH FOR THE STUDY OF VOLATILE PROFILE IN X-RAY IRRADIATED SURFACE-RIPENED CHEESES

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Food irradiation is a preservation procedure that consists in exposing foodstuffs to doses of ionising radiations, such as X-ray, γ-ray and electron beams[1]. The irradiation of surface mould-ripened soft cheese, such as Brie and Camembert, could be an alternative to traditional thermal pasteurisation to guarantee the microbiological safety and prolong shelf-life of such cheeses. To date, few analytical investigations have been carried out on the effects of X-ray irradiation treatment on the volatile profile of soft cheeses[1,2]. Hence, volatolomic studies about the cheese fingerprint modified from the irradiation and the related outcomes can be useful to identify potential markers of treatment. In this study, X-ray irradiation was applied to Brie and Camembert-type cheeses produced with cow milk and the modifications in the composition of volatile organic compounds have been investigated. HS-SPME technique combined with GC-MS was used to extract and analyse the volatile fraction from the dairy matrices. A Central Composite Design for Response Surface Methodology was employed to optimise the HS-SPME parameters in terms of extraction temperature, extraction time and sample amount. Hence, the best conditions were applied to non-irradiated and X-ray irradiated samples at three dose levels (2.0, 4.0 and 6.0 kGy) and the differences have been evaluated by means of a chemometric discrimination. Principal Component Analysis and Partial Least Square-Discriminant Analysis were used to discriminate the variation of volatile profiles among non-irradiated and irradiated samples. The outcomes demonstrated that the X-ray irradiation treatment differently affected the volatile classes of aroma Brie and Camembert-type cheeses. Finally, the results could be useful to identify potential markers of X-ray treatment for control purposes of irradiated soft cheeses.

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Acknowledgements:

This work is supported by funding from the Ministero della Salute, Project code GR-2018-12367064.

ALI-P7

A HIGH-SENSITIVE ANALYTICAL METHOD FOR THE DETERMINATION OF PAHS IN INFANT FOOD

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Polycyclic Aromatic Hydrocarbons (PAHs) are environmental pollutants which can contaminate several types of food. Their presence in specific foodstuffs can also be due to particular cooking practices (i.e., grilling, smoking, etc.). PAHs are mutagenic and carcinogenic[1], thus the European Union and the US Environmental Protection Agency (EPA) added these compounds in the priority list of pollutants, so that their presence in food must be steadily monitored. In Europe, the Regulation (EU) No. 915/2023 establishes maximum residue levels (MRLs) for PAHs in food products[2].

Infants and children are particularly vulnerable to the effects due to prolonged exposure to contaminants. For this reason, the maximum permitted level of PAHs in infant food is 1.0 µg kg^{-1}. In this regard, the official activities of food control need of analytical methods characterized by high sensitivity. The aim of this study was the optimization and validation of a novel analytical method for the detection and quantification of 4 PAHs (benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene) in baby food, based on QuEChERs method with dispersive solid phase extraction and GC-MS/MS analysis. The full validation dataset was evaluated by comparing data using Box Plot which is a very useful tool of graphic representation used for managing quantitative data and to optimize analytical methods. In this regard, the capability of comparing many distributions in the same graph, highlighting the most significant characteristics such as symmetry, range, variance and possible outliers can be considered as the main strength of such tool. Validation parameters such as specificity, linearity, LODs and LOQs, precision, recovery and ruggedness were determined, confirming the reliability of this method for accurate determinations of PAHs with very high sensitivity, so applicable to infant food analysis. The results of a monitoring are also discussed.

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Acknowledgements:

This work was supported by the Italian Ministry of Health (Rome, Italy) who funded the project code: IZS PB 08/20 RC.

ALI-P8

SYNTHESIS OF MOLECULARLY IMPRINTED POLYMER (MIP) FOR THE SELECTIVE EXTRACTION OF PHYTOSTEROLS IN FOOD MATRICES.

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Phytosterols (PSs) are bioactive compounds structurally and functionally similar to cholesterol. They contain an extra methyl, ethyl group, or double bond, and most of their side chains contain 9-10 carbon atoms. PSs have been classified as 4-desmethyl sterols of the cholestan series, which all have double bonds at the C_5 position of the B-ring[1]. These molecules are particularly known for widely range of properties including reduced intestinal cholesterol absorption and potential contributions to the prevention of cardiovascular diseases[2]. PSs are generally classified into three groups based on the number of methyl groups on carbon-4, two (4-dimethyl), one (4-monomethyl), or none (4-desmethyl). Moreover, 4-dimethyl esters and 4-monomethylsterols are metabolic intermediates in the biosynthetic pathway leading to the final product, 4-desmethyl phytosterols, but are usually present at low levels in most plant tissues. These compounds are present in plants, such as seeds, grains and legumes, both in free and conjugated form and they can be found in the form of fatty acyl esters, glycosides and fatty acyl glycosides. The selectivity issue in plant matrices is a challenging task, and classic approach such as solvent or solid phase extraction (SPE) are expensive and not always give the needed selectivity[3]. In this scenario a low cost molecularly imprinted polymers (MIPs) approach for the selective of extraction these compounds was not fully explored. In this work, a fast chemical MIPs synthesis approach for selective extraction of PSs was performed, using cholesterol as a dummy template. The MIPs were used as an adsorbent phase for SPE and combined with a targeted approach using liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) with atmospheric pressure chemical ionization (APCI). The results showed high selectivity with significant extraction performances and low matrix effect, a principal goal in complex plant matrices. The proposed strategy can be considered as fast and effective method to produce MIPs as extraction tool for the determination of these target compounds.

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ALI-P9

LIPIDOMICS AND METABOLOMIC TOOLS FOR THE CHARACTERIZATION OF CAMEMBERT CHEESE ANALYSED BY UHPLC-Q-ORBITRAP-MS

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Polar lipids (PLs) are macronutrients present in dairy products, known to have beneficial effects in cardiovascular functionality[1]. In this study, omics approaches were used to explore the PLs extracted from Camembert, a mould surface-ripened cheese of French origin. Workflow based on Folch lipid extraction and UHPLC-Orbitrap-MS analysis, integrated with metabolomic study, was performed with the aim of identifying and characterizing PLs[2]. The LipidSearch™ software was used for reliable and accurate molecular identification of 10 lipid subclasses, distinguished in ceramides (Cer), hexosyl ceramides (HexCer), phosphatidic acids (PA), phosphatidylcholines (PC), lysophosphatidylcholines (LPC), phosphatidylethanolamines (PE), lysophosphatidylethanolamine (LPE), phosphatidylinositols (PI), phosphatidylserines (PS) and sphingomyelins (SM). The open-source software MetaboAnalyst 5.0[3] was used to inspect the lipidomic dataset. Over Representation Analysis (ORA) in Metabolite Set Enrichment Analysis (MSEA) was performed with HMDB code associated to each PLs. After MSEA 5 metabolites, Cer(d18:1/16:0), Cer(d18:1/24:0), GlcCer(d18:1/16:0), Cer(d18:1/22:0) and GlcCer(d18:1/24:0) were significantly enriched ($p < 0.05$) in 9 organs or tissues (bone marrow, spleen, pancreas, skeletal muscle, skin, muscle, placenta, epidermis, intestine). The metabolite enrichment ratio was 28.571 in bone marrow and 5.862 in spleen, while other ratios were less than 4. The pathway analysis, performed on *Bos taurus* library, revealed that PLs were engaged in 8 metabolisms. In particular glycerophospholipid metabolism (hit rate, 5/36) and sphingolipid metabolism (hit rate, 4/21) were the two dominant pathways involving PC, PE, PS, LacCer, GlcCer and SM lipids. These results show that lipidomics and metabolomics are efficient tools for characterization of polar lipids extracted from dairy products.

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Acknowledgements:
This work is supported by funding from the Ministero della Salute, Project code GR-2018-12367064.

ALI-P10

CHARACTERIZATION OF *HELIX ASPERSA ASPERSA* FLAVOUR: NUTRITIONAL AND POLLUTION EVALUATION

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Helix aspersa is a phytophagous pulmonated gastropod mollusk, which is also detritivorous and occupies various levels in food chains[1]. In certain countries, humans consume *H. aspersa* as part of their diet. Additionally, *H. aspersa* is commonly bred for gastronomic or cosmetic purposes, specifically for slime production. However, the current methods of stimulating slime production often involve less invasive manual systems or more efficient equipment that, however, could lead to the death of the gastropods. Considering the potential future utilization of waste products from the supply chain, which may include gastropods unsuitable for the cosmetic or food industry, this study aimed to evaluate the nutritional properties of flours (fatty acids profile, fat matter, proteins, aminoacidic profile) obtained from snails bred in Italy on an organic farm for slime production purposes. Furthermore, laboratory-produced flour samples were analyzed to ensure the absence of organic pollutants, such as PAH, PCB, and PBDE since these mollusks are capable of accumulating contaminants present in the soil and air[1,2,3].

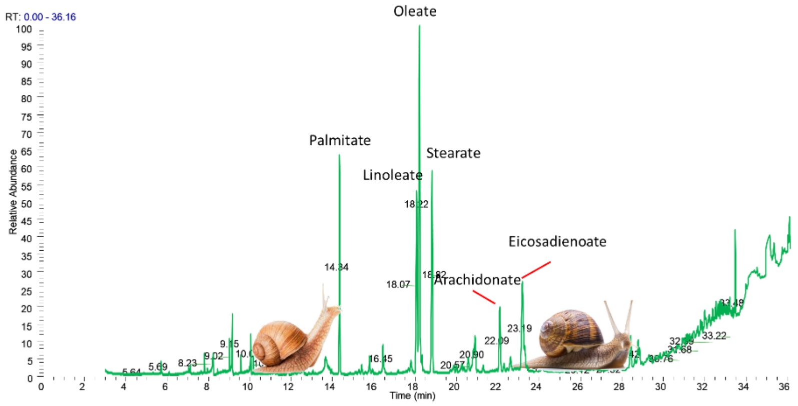

Figure 1: GC/MS chromatogram of *Helix aspersa* flour FAMEs.

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ALI-P11

INTEGRATED ANALYTICAL APPROACH FOR THE CHARACTERIZATION OF BIO-BASED FOOD CONTACT MATERIALS

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Bio-based materials, i.e., alternative materials to conventional plastics intended for food contact, are mainly based on the use of cellulose, wood, or biopolymers. Bio-based materials are commonly perceived as “green” and safe by consumers; however, their natural origin does not exclude the presence of harmful molecules[1,2], due to the use of additives, coating or surface treatments or the combination with different layers, to improve their performance. Their safety as food contact materials (FCMs) has still to be thoroughly demonstrated since the presence of harmful substances migrating from bio-based items has been recently evidenced[3]. Taking into account that standard protocols and official guidelines are still missing, the identification and determination of the compounds released from FCMs is an open challenge. In this context, the development of reliable analytical methods and protocols plays a key role in assessing the suitability of materials for food contact purposes. In this study, the integration of multiple approaches based on different analytical techniques such as gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-electrospray-mass spectrometry (LC-ESI-MS), attenuated total reflection-infrared spectroscopy (ATR-FTIR), and environmental scanning electron microscopy (ESEM), was proposed to obtain complementary information on commercially available FCMs. ATR-FTIR and ESEM were used for surface chemical composition and morphology characterization, respectively. Untargeted analysis carried out by GC-MS and LC-ESI-MS on the ethanol extracts of the materials investigated allowed the identification of different plasticizers, monomers, and surfactants occurring in adhesives used in multilayer materials or in glue for paper and plastic. By-products of poly-condensation reactions were also detected. Taking into account that these materials are intended to come into contact with food, these results can be valuable to estimate human exposure to possible health-threatening contaminants.

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Acknowledgements:

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RICE HUSK AS A SUSTAINABLE SOLUTION FOR SOIL REMEDIATION: FEASIBILITY AND PRACTICAL APPLICATION

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Rice husk is a waste by-product of rice production.[1] This material has a moderate cost and is readily available, representing 20-22% of the biomass produced by rice cultivation.[2] This study focused on the properties of rice husk in relation to the remediation of soils contaminated by potentially toxic elements (PTEs). The effect of particle size, pH, and the presence of ligands on sorption efficiency was evaluated for Cd, Cu, and Mn as PTEs. Furthermore, the possibility of regeneration and reuse of the material was attempted to be proven. The continuous flow method was used to select suitable operative conditions and maximize the retention of PTEs. Subsequently, pot experiments were conducted by growing two broadleaf plants, *Lactuca sativa,* and *Spinacia oleracea*, in aliquots of soil collected in a Piedmont site heavily contaminated by Cu, Cr, and Ni. Rice husk was added to the contaminated soil to evaluate its effectiveness in chemically immobilizing PTEs. The availability of Na, Mg, K, Al, Cr, Fe, Mn, Ni, Cu, Zn, Cd, and Pb was studied using Tessier's sequential extraction protocol: the fraction of mobile species, which potentially is the most harmful to the environment, was much higher than that normally present in unpolluted soils. The content of the aforementioned elements was also analyzed in plants and the uptake of PTEs was evaluated in relation to the addition of rice husk. It was shown that the growth of both plants was more efficient in the presence of rice husk due to its ability to reduce the mobility of PTEs in the soil. It was also shown that no heat or chemical treatments were required to achieve significant soil remediation results for the cultivation of these plant species. The simplicity, cost-effectiveness, and scalability of the use of rice husk make it suitable for practical applications in contaminated soils.

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Acknowledgements:

This study was conducted within the Agritech National Research Center and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4 – D.D. 1032 17/06/2022, CN00000022). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

ADVANCING MOSH/MOAH ANALYSIS TOWARDS SPECIATION AND CONTAMINANT IDENTIFICATION

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Contamination of food products attributed to mineral oil (MO), consisting of saturated (MOSH) and aromatic (MOAH) hydrocarbons, has been for years at the center of attention for its potential impact on consumers' health. The presence of aromatic compounds raises particular concern for increased risks due to their known toxicity and suspect carcinogenicity and genotoxicity, especially for species with 3 or more aromatic rings and low alkylation degree. Current reference methodologies, based on the LC-GC-FID hyphenation, allow separate quantification of the aliphatic and aromatic contaminant fractions. Nevertheless, the task is challenging due to matrix variety and complexity as well as for the presence of interferences. Furthermore, FID detection does not permit to obtain qualitative information about the type of MOSH or MOAH present, to distinguish between MOSH and hydrocarbons of synthetic origin, and to confirm or not the occurrence of synthetic hydrocarbons such as polyolefins (POH) or hydrocarbons of endogenous origin (terpenes, olefins residues, etc.).

As a consequence, laboratories tasked with MOSH/MOAH analysis would strongly benefit from advanced analytical tools capable of in-depth characterization for samples found positive to contamination. This contribution presents a two-dimensional platform for MOSH/MOAH analysis based on a preliminary HPLC separation followed by comprehensive gas chromatography (GC×GC) with parallel FID detection and high-resolution mass spectrometry. This solution can increase characterization capability and deliver a more insightful classification of the hydrocarbon profiles and act as confirmatory tool to classify contamination. A real-life case study highlights the value added for a identification of contamination origin in extra-virgin olive oil.

Acknowledgements:

This research was financed by the following Italian associations of the olive oil supply chain: Associazione Italiana Frantoiani Oleari (AIFO), Associazione Italiana dell'Industria Olearia (ASSITOL), Associazione Frantoi Oleari Italiani (ASSOFRANTOI), Federazione Nazionale del Commercio Oleario (FEDEROLIO), Filiera Olivicola-Olearia Italiana (FOOI), Italia Olivicola Società Consortile, Unione Nazionale Associazioni Produttori Olivicoli (UNAPOL), and by SRA Instruments S.p.A., Chelab S.r.l. and ALS Italia S.r.l. This work has been published: L. Menegoz Ursol et al. (2023). Food Chemistry, 406, 135032

ALI-P14

FAST SYNTHESIS OF MOLECULARLY IMPRINTED POLYMERS FOR THE DETERMINATION OF AFLATOXINS IN SUPPLEMENT FOODS

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Aflatoxins (AFs) are fungi secondary metabolites produced by the Aspergillus family. These compounds can enter in the food chain through different contamination sources, representing a risk to human health[1-3]. Commercial immunoaffinity columns are widely used for the extraction and cleanup of AFs from food samples[4]; however, their high cost and large solvent consumption create a need for alternative strategies. In this work, an alternative strategy for producing molecularly imprinted polymers (MIPs) was proposed to extract aflatoxins AFB1, AFB2, AFG1, and AFG2 from complex food samples, using liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS) for analysis. The MIPs were synthesized via a low-cost and rapid (5 min) sonochemical free-radical polymerization, using 1-hydroxy-2-naphthoic acid as a dummy template. To this aim, we tested acrylamide (AA), methacrylic acid (MAA), methacrylamide (MMA), and methacrylic acid +2-vinylpyridine (MAA-VP) as monomers, using ethylene glycol dimethacrylate (EGDMA) as the cross-linker and 2,2 azobisisobutyronitrile (AIBN) as the initiator. MMA-MIP based in solid phase extraction (SPE) yielded the best result than the others. For this reason, the performance of MIP-SPE was tested on 17 heterogeneous dietary supplements (i.e., Ginger, Echinacea purpurea, ginseng, hypericum, red elm, saffron, mango, red rice, parsley, red fruits, grapefruit, magnolia, Tilia cordata, Salsapariglia root, Hop, Verbena officinalis, and Galega officinalis) obtaining satisfactory recovery rates (65–90%) and high reproducibility (RSD < 6%). The selectivity towards other mycotoxins was proved and the obtained data were comparable with commercial immunoaffinity columns. So the proposed strategy can be considered a promising alternative to the classical immunoaffinity columns, being quite cheaper, but also demonstrating to be comparable in terms of performances.

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