



UNIVERSITÀ  
DEGLI STUDI DI TRIESTE

## Atti del XXV Congresso della Divisione di Chimica Analitica della Società Chimica Italiana

*Trieste, 13 – 17 Settembre 2015*

*[www.analitica2015.it](http://www.analitica2015.it)*





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## Presentazione

Il Congresso che la Divisione di Chimica Analitica della Società Chimica Italiana organizza annualmente vuole essere un punto d'incontro e di confronto per tutti coloro che svolgono la propria attività nella ricerca chimico analitica.

Il XXV Congresso si svolge da domenica 13 a giovedì 17 Settembre 2015 a Trieste, presso l'edificio H3 dell'Università degli Studi e si articola in sessioni scientifiche volte a coprire i principali settori della Chimica Analitica.

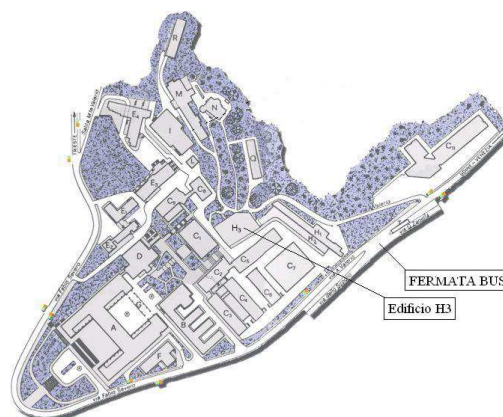
I principali argomenti di discussione sono i seguenti:

- 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

L'organizzazione è curata dal gruppo di Chimica Analitica dell'Università degli Studi di Trieste in collaborazione con diversi ricercatori di altre aree scientifiche e con l'importante contributo degli Atenei di Udine, Venezia (Ca' Foscari) e Padova.

## Sede del Congresso

**Edificio H3**, Università degli Studi di Trieste  
TRIESTE, via Valerio, 12/2  
(comprensorio P.le Europa)



# Programma

# XXV Congresso della Divisione di Chimica Analitica della SCI

Trieste, 13-17 Settembre 2015

## PROGRAMMA

### Domenica 13 Settembre 2015

*Hotel Savoia Excelsior Palace (Riva del Mandracchio, 4)*

17.00-21.00 Registrazione dei partecipanti

18.30-20.30 Cocktail di benvenuto

### Lunedì 14 Settembre 2015

*Aula Magna (ed. H3)*

dalle 8.30: Registrazione dei partecipanti

#### **Sessione Plenaria**

*Aula Magna (ed. H3)*

9.00-9.30 **Apertura del Congresso e saluti delle Autorità:**  
Edoardo Reisenhofer (Presidente Onorario del Congresso)  
Giuseppe Palleschi (Presidente della Divisione di Chimica di Analitica-SCI)  
Luigi Dei (Magnifico Rettore Eletto dell'Università di Firenze)  
Maurizio Fermeglia (Magnifico Rettore dell'Università di Trieste)  
Roberto Cosolini (Sindaco della Città di Trieste)

Conferenza Plenaria (*Presiede: Luigi Mondello*)

9.30-10.15 **PL1 IONIC LIQUIDS IN SEPARATIONS AND MASS SPECTROMETRY**  
D. W. Armstrong  
Robert A. Welch Professor, University of Texas at Arlington, Arlington, TX 76019



Conferenza Vincitore del Premio Giovane Ricercatore (*Presiede: Giuseppe Palleschi*)

10.15-10.45 **GR1** OMIC ANALYSIS OF DIFFERENT COMPLEX SAMPLES: A CHALLENGING BUT POWERFUL APPROACH  
A.L. Capriotti  
Dipartimento di Chimica, Università di Roma “La Sapienza”, Piazzale A. Moro, 5 – 00185 Roma

10.45-11.00 **Coffee break**

Sessione Parallela: **Scienza delle Separazioni 1 (SEPA1)**  
*Aula Magna (ed. H3)*  
(*Presiede: Luigi Mondello*)

11.10-11.40 **KN1** ON THE KINETIC PERFORMANCE OF COLUMNS PACKED WITH NEW 1.9 MM FULLY POROUS PARTICLES OF NARROW PARTICLE SIZE DISTRIBUTION  
A. Cavazzini<sup>1</sup>, M. Catani<sup>1</sup>, N. Marchetti<sup>1</sup>, L. Pasti<sup>1</sup>, D. Bell<sup>2</sup>, F. Gasparrini<sup>3</sup>  
<sup>1</sup>Department of Chemistry and Pharmaceutical Sciences, University of Ferrara, via L. Borsari 46, 44121, Ferrara, Italy  
<sup>2</sup>David S. Bell, Analytical Research and Services. Sigma-Aldrich/Supelco, 595 North Harrison Road. Bellefonte, PA 16823  
<sup>3</sup>Department of Drug Chemistry and Technology, “Sapienza” University of Rome, P.le Aldo Moro 5, 00185 Roma, Italy

11.40-12.00 **SEPA-1** PRACTICAL APPLICATIONS OF THE SOLVOPHOBIC THEORY TO THE ANALYTICAL SEPARATION OF BIOMOLECULES BY REVERSED PHASE HPLC  
D. Corradini, I. Nicoletti, I. Molnár  
National Research Council, Institute of Chemical Methodologies, Area della Ricerca di Roma 1, 00015 Montelibretti, Rome, Italy, Molnár-Institute Schneeglockchenstrasse 47, 10407 Berlin, Germany.

12.00-12.20 **SEPA-2** QUALITY BY DESIGN MEETS COMBINATION DRUGS: SIMULTANEOUS DETERMINATION OF CAPTOPRIL, HYDROCHLOROTHIAZIDE AND THEIR IMPURITIES BY CAPILLARY ELECTROPHORESIS  
B. Pasquini, S. Orlandini, C. Caprini, M. Del Bubba, M. Innocenti, S. Pinzauti, S. Furlanetto  
Dipartimento di Chimica “U. Schiff”, Università di Firenze, via U. Schiff 6-Via della Lastruccia 3 – 50019 Sesto F.no (FI)

12.20-12.40 **SEPA-3** POLYCYCLIC AROMATIC HYDROCARBONS DETERMINATION IN WATER: A COMPARISON BETWEEN “DRAW-EJECT” AND “EXTRACT-DISCARD” METHODS USING MICROEXTRACTION BY PACKED SORBENT COUPLED WITH GASCHROMATOGRAPHY – MASS SPECTROMETRY.

M. Quinto<sup>1</sup>, D. Centonze<sup>1</sup>, C. Palermo<sup>1</sup>, D. Nardiello<sup>1</sup>, G. Spadaccino<sup>1</sup>, D. Li<sup>2</sup>

<sup>1</sup>Department SAFE — Department of Science of Agriculture, Food and Environment, University of Foggia, via Napoli 25, I-71100 Foggia, Italy

<sup>2</sup>Key Laboratory of Natural Resource of the Changbai Mountain and Functional Molecular (Yanbian University), Ministry of Education, Park Road 977, Yanji City, Jilin Province, China

12.40-13.00 **SEPA-4 QUALITATIVE AND SEMI-QUANTITATIVE ANALYSIS OF PHOSPHOLIPIDS IN RAT LIVER MITOCHONDRIA SAMPLES BY HPLC-IT/TOF-MS**

C. Fanali<sup>1</sup>, L. Dugo<sup>1</sup>, A.M. Sardanelli<sup>1,2</sup>, A. Gnoni<sup>2</sup>, F. Cacciola<sup>3</sup>, M. Oteri<sup>4</sup>, M. Beccaria<sup>4</sup>, L. Mondello<sup>1,4</sup>

<sup>1</sup>Centro Integrato di Ricerca(C.I.R.), Campus-Biomedico University, Via Álvaro del Portillo, 21, 00128 - Roma, Italy;

<sup>2</sup>Department of Basic Medical Sciences, Neurosciences and Sensory Organs, University of Bari Aldo Moro - Bari, Italy;

<sup>3</sup>"Scienze dell'Ambiente, della Sicurezza, del Territorio, degli Alimenti e della Salute" Department, University of Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy.

<sup>4</sup>Dipartimento di Scienze del Farmaco e dei Prodotti per la Salute, University of Messina, viale Annunziata, 98168 – Messina, Italy.

Sessione Parallela: **Beni Culturali (BBCC)**

**Aula 1A (ed. H3)**

(*Presiede: Luigia Sabbatini*)

11.00-11.20 **BBCC-1 A 'CLEAN & CHECK' METHOD FOR THE SIMULTANEOUS RECOGNITION OF ALBUMEN AND YOLK BY BIOSENSING: APPLICATION IN CULTURAL HERITAGE CONSERVATION**

S. Scarano<sup>1</sup>, E. Carretti<sup>1,2</sup>, P. Baglioni<sup>1,2</sup>, L. Dei<sup>1,2</sup>, and M. Minunni<sup>1,2</sup>

<sup>1</sup>Laboratorio Sensori e Biosensori, Dipartimento di Chimica 'Ugo Schiff', Università degli Studi di Firenze, via della Lastruccia 3-13, Sesto Fiorentino, 50019, Firenze, Italy.

<sup>2</sup>Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, CSGI - Dipartimento di Chimica, Università degli Studi di Firenze, via della Lastruccia 3-13, Sesto Fiorentino, 50019, Firenze, Italy.

11.20-11.40 **BBCC-2 APULIAN RED FIGURED POTTERY FROM TARANTO (SOUTHERN ITALY). NON LINEAR STATISTICAL METHOD TO CAPITALIZE CHEMICAL DATA IN ARCHAEOLOGY.**

L.C. Giannossa<sup>1</sup>, R. M. Mininni<sup>2</sup>, A. Bitetto<sup>2</sup>, G. Giannelli<sup>1</sup>, C. Taccogna<sup>3</sup>, R. Laviano<sup>3</sup>, A. Mangone<sup>1</sup>

<sup>1</sup>Dipartimento di Chimica, Università degli Studi Bari Aldo Moro, Via Orabona 4 – 70126 Bari

<sup>2</sup>Dipartimento di Matematica, Università degli Studi Bari Aldo Moro, Via Orabona 4 – 70126 Bari

<sup>3</sup>Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi Bari Aldo Moro, Via Orabona 4 – 70126 Bari

- 11.40-12.00 **BBCC-3 OILS USED IN MODERN OIL-BASED PAINT MEDIA: A COMPREHENSIVE STUDY BY MASS SPECTROMETRY**  
 E. Ghelardi<sup>1</sup>, J. La Nasa<sup>1</sup>, I. Degano<sup>1</sup>, F. Modugno<sup>1</sup>, M.P. Colombini<sup>1,2</sup>  
<sup>1</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13 – 56124 Pisa  
<sup>2</sup>Institute for the Conservation and Promotion of Cultural Heritage, CNR, via Madonna del Piano, 10 – 50019 Sesto Fiorentino (FI)
- 12.00-12.20 **BBCC-4 DETECTING DYES ON MICRO-SAMPLES FROM THE CULTURAL HERITAGE - A CHALLENGE FOR SURFACE ENHANCED RAMAN SPECTROSCOPY**  
M. Gulmini<sup>1</sup>, A. Idone, P. Davit, E. Diana, L. Anfossi, E. Prenesti, M. Aceto<sup>2</sup>  
<sup>1</sup>Dipartimento Chimica, Università degli Studi di Torino, Via Giuria, 5 – 10124 Torino, Italy  
<sup>2</sup>Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale, Viale Michel, 11 - 15121 Alessandria, Italy
- 12.20-12.40 **BBCC-5 MOLECULAR TRACERS OF HUMAN SETTLEMENT AND AGRICULTURAL ACTIVITY IN SEDIMENTARY RECORDS**  
E. Argiriadis<sup>1</sup>, D. Battistel<sup>1</sup>, T. Kirchgeorg<sup>1</sup>, M. Vecchiato<sup>1</sup>, N. M. Kehrwald<sup>1</sup>, C. Barbante<sup>1,2</sup>  
<sup>1</sup>Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari Venezia, Dorsoduro 2137, Calle Larga Santa Marta – 30123 Venezia  
<sup>2</sup>Istituto per le Dinamiche dei Processi Ambientali (IDPA-CNR), Dorsoduro 2137, Calle Larga Santa Marta – 30123 Venezia
- 12.40-13.00 **BBCC-6 FURTHER THERMAL ANALYTICAL AND CHEMOMETRIC TESTS ON HUMAN FOSSIL BONES FROM TWO NECROPOLISES IN NORTHERN SUDAN**  
M. Tomassetti, F. Marini, R. Bucci, L. Campanella, A. Coppa  
 Dipartimento di Chimica, Università di Roma “La Sapienza”, Piazzale A. Moro, 5 – 00185 Roma, Italia.
- 13.00-14.00 **Pranzo** (*edificio I*)
- 14.00-15.00 **SESSIONE POSTER P1: P01-P57 (ALI-BBCC-CHEM-MASSA-SEPA)**

Sessione Parallela: **Spettrometria di Massa (MASSA)**

*Aula Magna (ed. H3)*

(*Presiede: Maria Careri*)

- 15.10-15.30 **MASSA-1 STUDY OF PHOTOCHEMICAL TRANSFORMATION OF TWO SUNSCREENS IN SURFACE WATERS BY HRMS**  
 P. Calza, D. Vione, D. Fabbri, C. Medana, C. Minero

<sup>1</sup>Dipartimento di Chimica, Università di Torino, Via P. Giuria, 5 – 10125 Torino

<sup>2</sup>Dipartimento di Biotecnologie Molecolari e Scienze per la salute, Università di Torino, via P. Giuria, 5 – 10125 Torino

15.30-15.50 **MASSA-2 BROMINATED FLAME RETARDANTS IN EDIBLE BIVALVES: FOOD CONTROL AND LACK OF SPECIFIC LEGISLATION**

S. Pizzini<sup>1</sup>, R. Piazza<sup>2,1</sup>, G. Cozzi<sup>1</sup>, C. Barbante<sup>1,2</sup>

<sup>1</sup>Institute for the Dynamics of Environmental Processes, National Research Council (CNR-IDPA), Dorsoduro 2137, 30123 Venice, Italy

<sup>2</sup>Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Dorsoduro 2137, 30123 Venice, Italy

15.50-16.10 **MASSA-3 A NEW CLASS OF MALDI MATRICES FOR HARDLY IONIZABLE COMPOUNDS BASED ON SUPERBASIC ALKYL-SUBSTITUTED BISPHTHAZENE PROTON SPONGES**

C.D. Calvano<sup>1,2</sup>, A. Monopoli<sup>1</sup>, C. Chiapperino<sup>1</sup>, J. Sundermeyer<sup>2</sup>, T.R.I. Cataldi<sup>1,2</sup>, F. Palmisano<sup>1,2</sup>

<sup>1</sup>Dipartimento Chimica, <sup>2</sup>Centro di Ricerca Interdipartimentale S.M.A.R.T., Università degli Studi di Bari Aldo Moro, via Orabona 4, 70126 Bari (Italy),

<sup>2</sup>Fachbereich Chemie Philipps-Universität, Marburg (Germany)

16.10-16.30 **MASSA-4 HRMS ANALYSIS OF ORGANIC FRACTION IN PM<sub>2.5</sub>: POST-RUN DATA ANALYSIS WORK FLOW AND THE ROLE OF IONIZATION SOURCE.**

C. Bortolini<sup>1</sup>, A. Zielinski<sup>2</sup>, I. Kourtchev<sup>2</sup>, S. Bogialli<sup>1</sup>, M. Kalberer<sup>2</sup>.

<sup>1</sup>Department of Chemical Sciences, University of Padua, Via Marzolo 1 - 35131 Padua, Italy

<sup>2</sup>University of Cambridge, Cambridge CB2 1EW, United Kingdom

16.30-16.50 **Coffee break**

16.50-17.10 **MASSA-5 IDENTIFICATION OF ISOBARIC PHOSPHOLIPIDS IN SEAFOOD: THE KEY ROLE OF HIGH RESOLUTION MASS SPECTROMETRY**

S. Granafei<sup>1</sup>, I. Losito<sup>1,2</sup>, F. Palmisano<sup>1,2</sup>, T.R.I. Cataldi<sup>1,2</sup>

<sup>1</sup>Dipartimento di Chimica, <sup>2</sup>Centro di Ricerca Interdipartimentale S.M.A.R.T., Università degli Studi di Bari "Aldo Moro", Via E. Orabona 4, 70126 Bari

17.10-17.30 **MASSA-6 ANALYTICAL STRATEGIES TOWARDS THE ASSESSMENT OF "GLUTEN-FREE" PRODUCT SAFETY: LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY vs IMMUNOSENSING**

M. Mattarozzi<sup>1</sup>, A. Manfredi<sup>1</sup>, A. Masutti<sup>1</sup>, M. Giannetto<sup>1,2</sup>, C. Mucchino<sup>1</sup>, M. Careri<sup>1,2</sup>

<sup>1</sup>Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze, 17/A – 43124 Parma

<sup>2</sup>Centro Interdipartimentale SITEIA.PR, Università degli Studi di Parma, Parco Area delle Scienze, 181/A – 43124 Parma

17.30-17.50 **MASSA-7 IDENTIFICATION OF ACTIVE SPECIES FROM A PLANT EXTRACT AGAINST CANCEROUS CELL**

PROLIFERATION: A MICRO LC-MS/MS STUDY

F. Gosetti<sup>1</sup>, S. Martinotti<sup>1</sup>, B. Bolfi<sup>1</sup>, E. Mazzucco<sup>1</sup>, E. Ranzato<sup>1</sup>, E. Manfredi<sup>1,2</sup>, E. Marengo<sup>1</sup>

<sup>1</sup>Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, Viale T. Michel, 11 – 15121 Alessandria

<sup>2</sup>ISALIT S.r.l., Via G. Bovio, 6 – 28100 Novara

- 17.50-18.10 **MASSA-8** HIGH RESOLUTION MASS SPECTROMETRY COUPLED TO UHPLC AS A TOOL FOR THE UNEQUIVOCAL IDENTIFICATION OF ESTROGEN METABOLITES IN MILK  
S. Ventura, G. La Barbera, S. Stampachiacchiere, R. Samperi, A. Laganà  
Dipartimento di Chimica, Università di Roma Sapienza, Piazzale Aldo Moro 5, 00185 Roma

Sessione Parallela: **Chemimetria e Qualità del Dato (CHEM)**

**Aula 1A (ed. H3)**

(*Presiede: Silvia Lanteri*)

- 15.00-15.30 **KN2** USE AND ABUSE OF SIGNAL PRE-PROCESSING  
P. Oliveri, R. Simonetti, M.C. Casolino  
Dipartimento di Farmacia, Università di Genova, Via Brigata Salerno, 13 – 16147 Genova
- 15.30-15.50 **CHEM-1** RECENT ADVANCES IN CONSENSUS MODELLING OF MULTIPLE ANALYTICAL CHEMICAL DATA  
D. Ballabio<sup>1</sup>, V. Consonni<sup>1</sup>, M. Scampicchio<sup>2</sup>, R. Todeschini<sup>1</sup>  
<sup>1</sup>Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università Milano-Bicocca, P.zza della Scienza, 1 - 20126 Milano  
<sup>2</sup>Facoltà di Scienze e Tecnologie, Libera Università di Bolzano, piazza Università, 5 - 39100 Bolzano
- 15.50-16.10 **CHEM-2** SPARSE METHODS APPLIED TO HYPERSPECTRAL IMAGING: CLASSIFICATION OF ARABICA AND ROBUSTA GREEN COFFEE BEANS  
R. Calvini<sup>1</sup>, A. Ulrici<sup>1</sup>, J. M. Amigo<sup>2</sup>  
<sup>1</sup>Department of Life Sciences, University of Modena and Reggio Emilia, Padiglione Besta, Via Amendola 2, 42122 Reggio Emilia, Italy  
<sup>2</sup>Department of Food Science, Faculty of Sciences, University of Copenhagen, Rolighedsvej 30, DK-1958 Frederiksberg C, Denmark
- 16.10-16.30 **CHEM-3** DIFFERENT APPROACHES TO THE ANALYSIS OF DESIGNED NIR FINGERPRINTING DATA  
M. Cocchi<sup>1</sup>, A. Sandak<sup>2</sup>, J. Sandak<sup>2</sup>, F. Marini<sup>3</sup>  
<sup>1</sup>Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via Campi 103 – 41125 Modena  
<sup>2</sup>CNR-IVALSA, Via Biasi, 75 - 38010 San Michele all'Adige, Trento.  
<sup>3</sup>Dipartimento di Chimica, Università Roma La Sapienza, P.le A. Moro 5 – 00185 Roma.
- 16.30-16.50 **Coffee break**

- 16.50-17.10 **CHEM-4** LIMIT OF DETECTION AND QUANTIFICATION IN THE PRESENCE OF INSTRUMENTAL AND NON-INSTRUMENTAL ERRORS: STUDY OF THE POSSIBLE SOURCES OF ERROR AND APPLICATION TO THE ANALYSIS OF AT TRACE LEVELS BY ICP-MS TECHNIQUE  
D. Badocco, P. Pastore  
 Department of Chemical Sciences, University of Padua, Via Marzolo 1, 35131 Padua
- 17.10-17.30 **CHEM-5** THE COMBINATION OF RAPID ANALYTICAL PROFILING AND DATA FUSION CHEMOMETRIC TOOLS FOR THE IDENTIFICATION OF ADULTERATIONS AND FOR PROVEVANCE STUDIES OF DIFFERENT FOOD MATRICES  
E. Robotti, M. Bobba, E. Sangiorgi, E. Marengo  
 Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, Viale Michel 11, 15121 Alessandria
- 17.30-17.50 **CHEM-6** VALIDATION: STILL AN UNEXPLORED LAND?  
F. Marini<sup>1</sup>, F. Westad<sup>2</sup>  
<sup>1</sup>Dipartimento di Chimica, Università di Roma "La Sapienza", Piazzale Aldo Moro, 5 – 00185 Roma  
<sup>2</sup>CAMO Software AS, Nedre Vollgate 8 – 0158 Oslo (Norway)
- 17.50-18.10 **CHEM-7** ARRAYS OF HETEROGENEOUS SENSORS, CONTINUOUS MONITORING FOR DETECTION OF OLFACTORY NUISANCE AND SELF ORGANIZING MAPS  
P. Barbieri<sup>1</sup>, P. Posocco<sup>1</sup>, A. Fabbris<sup>2</sup>, G. Barbieri<sup>2</sup>, G. Adami<sup>1</sup>, S. Del Frate<sup>3</sup>, A. Pillon<sup>3</sup>, F. Sturzi<sup>3</sup>  
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<sup>2</sup>ARCo SolutionS srl, spin off del Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Piazzale Europa, 1 – 34127 Trieste  
<sup>3</sup>Agenzia Regionale per la Protezione dell'Ambiente del Friuli Venezia Giulia, via Cairoli 14, - 33057 Palmanova (UD)

***Aula Magna (ed. H3)***

- 18.15-20.00 **Assemblea della Divisione** con consegna del Premio Giovane Ricercatore, del Premio di Laurea e delle Medaglie della Divisione

# Martedì 15 Settembre 2015

## Sessione Plenaria

*Aula Magna (ed. H3)*

Conferenza Plenaria (*Presiede: Paolo Ugo*)

- 9.00-9.45 **PL2** OPENING NEW ANALYTICAL PATHWAYS WITH BIPOLAR ELECTROCHEMISTRY  
A. Kuhn  
Institut des Sciences Moléculaires, Université de Bordeaux, ENSCBP, 16 avenue Pey Berland, 33607 Pessac, France

## Sessione Parallela: **Elettroanalitica 1 (ELETTRO1)**

*Aula Magna (ed. H3)*

(*Presiede: Paolo Ugo*)

- 10.00-10.30 **KN3** CARBON BLACK AS SUCCESSFULL CARBONACEOUS NANOMATERIAL MODIFIER FOR SCREEN-PRINTED ELECTRODES  
F. Arduini<sup>1</sup>, A. Amine<sup>2</sup>, S. Cinti<sup>1</sup>, D. Talarico<sup>1</sup>, D. Moscone<sup>1</sup>, G. Palleschi<sup>1</sup>  
<sup>1</sup>Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy  
<sup>2</sup>Université Hassan II-Mohammedia, Faculté de Sciences et Techniques Laboratoire Génie des Procédés et Environnement, B.P. 146, Mohammadia, Morocco
- 10.30-10.50 **ELETTRO-1** ARRAYS OF COPPER NANOWIRE ELECTRODES FOR THE SENSITIVE ELECTROANALYSIS OF NITRATE  
A.M. Stortini, L.M. Moretto, P. Ugo  
Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155, 30172 Venezia Mestre.
- 10.50-11.10 **ELETTRO-2** SCANNING ELECTROCHEMICAL MICROSCOPY AND ANODIC STRIPPING VOLTAMMETRY TO CHARACTERISE SILVER NANOPARTICLES AT SOLID/SOLUTION INTERFACES  
G. Pecchielan, G. Bonazza and S. Daniele  
Dipartimento di Scienze Molecolari e Nanosistemi, Università Cà Foscari Venezia, Dorsoduro 2137, Calle Larga Santa Marta – 30123 Venezia
- 11.10-11.40 **Coffee break**
- 11.40-12.00 **ELETTRO-3** ANALYTICAL CHARACTERIZATION OF ELECTRO-DECORATED ZnO NANORODS FOR GAS SENSING APPLICATIONS  
E. Dilonardo<sup>1,2</sup>, M. Penza<sup>3</sup>, M. Alvisi<sup>3</sup>, C. Di Franco<sup>4</sup>, F.

Palmisano<sup>1</sup>, L. Torsi<sup>1</sup>, N. Cioffi<sup>1</sup>

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<sup>4</sup>CNR-IFN Bari, Via Amendola 173 70126 Bari, Italy.

12.00-12.20 **ELETTRO-4** ORGANIC SOLVENTS AS GATE MEDIUM IN ELECTROLYTE-GATED THIN FILM TRANSISTORS

P. Seshadri, K. Manoli, M. Singh, M. Magliulo, G. Palazzo, L. Torsi

Dipartimento di Chimica, Università degli studi di Bari Aldo Moro, Via Orabona 4, 70126, Bari, Italy

12.20-12.40 **ELETTRO-5** ELECTRODEPOSITION OF ALUMINIUM FROM IONIC LIQUIDS: CORROSION BEHAVIOR AND DEPOSITION PARAMETERS INFLUENCE

E. Berretti<sup>1</sup>, A. Giaccherini<sup>1</sup>, L. Cavaciocchi<sup>2</sup>, S. Caporali<sup>1</sup>, S. Furlanetto<sup>1</sup>, S. Orlandini<sup>1</sup>, B. Pasquini<sup>1</sup>, S. Bellandi<sup>1</sup>, S. Pinzauti<sup>1</sup> and M. Innocenti<sup>1</sup>

<sup>1</sup>Chemistry Department, University of Firenze, Firenze, Italy

<sup>2</sup>BluClad s.r.l., Prato

12.40-13.00 **ELETTRO-6** IN-SITU STRUCTURAL CHARACTERIZATION OF SEMICONDUCTOR THIN FILMS FOR SOLAR CELLS SYNTHESIZED BY E-ALD

A. Giaccherini<sup>1</sup>, S. Cinotti<sup>1</sup>, R.A. Picca<sup>2</sup>, F. Carlà<sup>3</sup>, G. Montegrossi<sup>4</sup>, F. Capolupo<sup>1</sup>, R. Felici<sup>3</sup>, F. Di Benedetto<sup>5</sup>, S. Furlanetto<sup>1</sup>, N. Cioffi<sup>2</sup>, A. Lavacchi<sup>6</sup>, M. Innocenti<sup>1</sup>

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<sup>3</sup>ESRF, Grenoble, Cedex, France

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<sup>5</sup>Department of Earth Sciences, University of Firenze, Firenze, Italy

<sup>6</sup>Institute of Chemistry of Organometallic Compounds, CNR, Firenze, Italy

Sessione Parallela: **Spettroscopia Analitica (SPETTRO)**

**Aula 1A (ed. H3)**

(*Presiede: Giuseppe Spoto*)

10.00-10.30 **KN4** EARLY DIAGNOSIS OF TROPONIN T BY OPTICAL, LABEL FREE, AND REAL TIME NANOSENSING. A HIGH SENSITIVE POINT-OF-CARE TESTING BY COUPLING EMERGING SYNTHETIC RECEPTORS TO LOCALIZED SURFACE PLASMON RESONANCE (LSPR)

S. Scarano

Dipartimento di Chimica 'Ugo Schiff', Università degli Studi di Firenze, Via



della Lastruccia 3, Sesto Fiorentino (FI), Italy.  
simona.scarano@unifi.it

- 10.30-10.50 **SPETTRO-1** LIGANDS IMMOBILIZED ON TRIACETYLCELLULOSE FILM TAPES FOR TRIVALENT AND BIVALENT METAL IONS SENSING  
R. Biesuz, S. Re, A.M. Tivelli, M. Pesavento, G. Alberti  
Dipartimento Chimica, Università di Pavia, via Taramelli 12 – 27100 Pavia
- 10.50-11.10 **SPETTRO-2** GROWTH INHIBITION OF *PSEUDOMONAS FLUORESCENS* BIOFILMS VIA ION BEAM SPUTTERED Ag/TEFLON COMPOSITE FILMS: A COMPARATIVE MORPHOLOGICAL AND SPECTROSCOPIC STUDY  
M.C. Sportelli<sup>1</sup>, E. Tütüncü<sup>2</sup>, R.A. Picca<sup>1</sup>, M. Valentini<sup>3</sup>, A. Valentini<sup>3</sup>, C. Kranz<sup>2</sup>, B. Mizaikoff<sup>2</sup>, N. Cioffi<sup>1</sup>  
<sup>1</sup>Dipartimento di Chimica, Università degli Studi di Bari “Aldo Moro”, V. Orabona, 4 – 70126 Bari, Italy.  
<sup>2</sup>Institute of Analytical and Bioanalytical Chemistry, Ulm University, Albert Einstein Allee, 11 – 89081 Ulm, Germany.  
<sup>3</sup>Dipartimento di Fisica, Università degli Studi di Bari “Aldo Moro”, V. Orabona, 4 – 70126 Bari, Italy.
- 11.10-11.30 **Coffee break**
- 11.30-12.00 **KN5** ANALYTICAL CHARACTERIZATION OF POLYURETHANE FOAMS MODIFIED BY SILVER NANOPHASES. A MULTI-TECHNIQUE APPROACH FOR THE SYSTEMATIC ASSESSMENT OF SURFACE CHEMISTRY, MORPHOLOGY, ION AND NANOPARTICLE RELEASE ISSUES  
R.A. Picca<sup>1</sup>, F. Paladini<sup>2</sup>, M.C. Sportelli<sup>1</sup>, M. Pollini<sup>2</sup>, L.C. Giannossa<sup>1</sup>, C. Di Franco<sup>3</sup>, A. Mangone<sup>1</sup>, A. Valentini<sup>4</sup>, A. Sannino<sup>2</sup>, N. Cioffi<sup>1</sup>  
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<sup>2</sup>Dipartimento di Ingegneria dell’Innovazione, Università del Salento, Via per Monteroni, 73100 Lecce  
<sup>3</sup>CNR-IFN - Dipartimento Interateneo di Fisica, Università degli Studi di Bari Aldo Moro, Via Orabona 4, 70126 Bari  
<sup>4</sup>Dipartimento Interateneo di Fisica, Università degli Studi di Bari Aldo Moro, Via Orabona 4, 70126 Bari
- 12.00-12.20 **SPETTRO-3** SURFACE PLASMON RESONANCE IMAGING DETECTION OF FOODBORNE PATHOGENS BY USING PNA PROBES AND GOLD NANOPARTICLES  
A.M. Aura<sup>1</sup>, R. D’Agata<sup>1</sup>, N. Bellassai<sup>2</sup>, C. Valenti<sup>2</sup>, G. Spoto<sup>1,2</sup>  
<sup>1</sup>Dipartimento di Scienze Chimiche, Università di Catania, Viale Andrea Doria, 6 - 95125 Catania  
<sup>2</sup>Consorzio I.N.B.B., Viale delle Medaglie d’Oro, 305- 00136 Roma
- 12.20-12.40 **SPETTRO-4** INSIGHTS INTO THE CHEMICAL VAPOR GENERATION OF CADMIUM AT TRACE LEVEL  
D. Angelini<sup>1,2</sup>, E. Pitzalis<sup>1</sup>, A. D’Ulivo<sup>1</sup>  
<sup>1</sup>C.N.R., Institute of Chemistry of Organometallic Compounds, UOS of Pisa,

Via Moruzzi, 1 Pisa (I)

<sup>2</sup>University of Pisa, Department of Chemistry and Industrial Chemistry, Via Moruzzi, 3 Pisa (I)

- 12.40-13.00 **SPETTRO-5** LA-ICP-MS MAPPING OF THE SILVER DISTRIBUTION IN SKIN DURING WOUND HEALING  
W.R.L. Cairns<sup>1</sup>, C. Rigo<sup>1</sup>, M. Roman<sup>2</sup>, I. Munivrana<sup>3</sup>, V. Vindigni<sup>3</sup>, E. Kolschen<sup>3</sup>, D.U. Solveig<sup>4</sup>, J. Feldmann<sup>4</sup>, B. Spence<sup>5</sup>, C. Barbante<sup>1</sup>.  
<sup>1</sup>Istituto per la Dinamica dei Processi Ambientali (IDPA-CNR), Dorsoduro 2137 - 30123 Venezia  
<sup>2</sup>Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari Venezia, Dorsoduro 2137 - 30123 Venezia  
<sup>3</sup>Centro Ustioni. Divisione di Chirurgia Plastica, Ospedale Universitario di Padova, Via Giustiniani 2 - 35128 Padova  
<sup>4</sup>Trace Element Speciation Laboratory, Meston Walk Aberdeen AB24 3UE Scotland UK  
<sup>5</sup>Teledyne CETAC European Business Office, 17 Clearwater Drive, West Didsbury, Manchester, M20 2ED, UK.

Sessione Parallela: **Equilibri in soluzione (EQUI)**

**Aula 0B (ed. H3)**

(*Presiede: Giuseppe Arena*)

- 10.00-10.30 **KN6** APPLICATIONS OF THE CHEMICAL EQUILIBRIUM MODELLING EXPERTISE  
P. G. Daniele  
Università di Torino, Dipartimento Chimica, via P. Giuria, 7 – 10125 Torino, Italy
- 10.30-10.50 **EQUI-1** SEQUESTERING ABILITY OF HYDROXYBENZOIC ACIDS TOWARDS ALUMINIUM(III) CATIONS: A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY  
E. Furia, T. Marino, A. Napoli, N. Russo, A. Tagarelli  
Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 87036 Rende (CS)
- 10.50-11.10 **EQUI-2** ANION INCAPSULATION BY Gd<sup>3+</sup>[15-METALLACROWN-5] COMPARTMENTS IN NEUTRAL AQUEOUS SOLUTION  
C. Sgarlata<sup>1</sup>, R. Migliore<sup>1</sup>, E. Trivedi<sup>2</sup>, V. L. Pecoraro<sup>2</sup>, G. Arena<sup>1</sup>  
<sup>1</sup>Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Via A. Doria, 6 – 95125 Catania; sgarlata@unict.it  
<sup>2</sup>Department of Chemistry, University of Michigan, Ann Arbor, 930 N. University Ave, Ann Arbor, Michigan 48109, United States
- 11.10-11.40 **Coffee break**
- 11.40-12.00 **EQUI-3** SEQUESTRATION OF DIFFERENT M<sup>n+</sup> CATIONS BY EDDS IN NATURAL FLUIDS  
C. Bretti, R.M. Cigala, F. Crea, G. Lando, S. Sammartano.  
Dipartimento di Scienze Chimiche, Università degli Studi di Messina, Viale

Ferdinando Stagno d'Alcontres, 31, I-98166 Messina (Vill. S. Agata), Italy.

12.00-12.20 **EQUI-4 THERMODYNAMIC STUDY ON TRIAZOLO-TRIAZOLE HETEROCYCLIC SYSTEMS**  
C. Manfredi<sup>1</sup>, R. Centore<sup>1</sup>, A. Peluso<sup>2</sup>, S. Volino<sup>1</sup>, P. Scarano<sup>1</sup>, I. Sorrentino<sup>1</sup>

<sup>1</sup>Dipartimento di Scienze Chimiche, Università di Napoli, Via Cintia 46, 80126 Napoli, Italia

<sup>2</sup>Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, Via Giovanni Paolo II 132, 84084, Fisciano (SA), Italia

12.20-12.40 **EQUI-5 CHARACTERIZATION OF PHOTOTRANSFORMATION PRODUCTS OF AMINO-ACIDS.**  
S. Berto<sup>1</sup>, E. De Laurentiis<sup>1</sup>, E. Chiavazza<sup>1</sup>, T. Tota<sup>1</sup>, P. G. Daniele<sup>1</sup>, M. Minella<sup>1</sup>, M. Isaia<sup>2</sup>, D. Vione<sup>1</sup>

<sup>1</sup>Università di Torino, Dipartimento Chimica, via P. Giuria, 7 – 10125 Torino, Italy

<sup>2</sup>Università di Torino, Dipartimento di Scienze della Vita e Biologia dei Sistemi, Via Accademia Albertina 13, Torino 10123, Italy

13.00-14.00 **Pranzo (edificio I)**

14.00-14.50 **SESSIONE POSTER P2: P58-P106 (FORE-ELETTRO-EQUI-SENSO-SPETTRO)**

Sessione Parallela: **Elettroanalitica2 (ELETTRO2)**

**Aula Magna (ed. H3)**

*(Presiede: Salvatore Daniele)*

15.00-15.20 **ELETTRO-7 "INHERENTLY CHIRAL" ELECTRODES: TOOLS FOR CHIRAL VOLTAMMETRY**  
P.R. Mussini<sup>1</sup>, S. Arnaboldi<sup>1</sup>, F. Sannicolò<sup>1</sup>, R. Martinazzo<sup>1</sup>, T. Benincori<sup>2</sup>, R. Cirilli<sup>3</sup>

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<sup>2</sup>Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Via Valleggio 11, 22100 Como

<sup>3</sup>Dipartimento del Farmaco, ISS, Via Regina Elena 299, 00161 Roma

15.20-15.40 **ELETTRO-8 SYNTHESIS AND CHARACTERIZATION OF "GREEN" METALLIC NANOPARTICLES FOR ELECTROCHEMICAL BIOSENSORS DEVELOPMENT**  
P. Bollella<sup>1</sup>, C. Tortolini<sup>1,3</sup>, G. Favero<sup>1</sup>, F. Mazzei<sup>1</sup>, L. Gorton<sup>2</sup>, R. Antiochia<sup>1</sup>

<sup>1</sup>Department of Chemistry and Drug Technologies, Sapienza University of Rome P.le Aldo Moro 5, 00185 – Rome, Italy

<sup>2</sup>Department of Analytical Chemistry/Biochemistry, P.O. Box 124, 221 00 – Lund, Sweden

<sup>3</sup>Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185 – Rome, Italy

15.40-16.00 **ELETTRO-9** CHARACTERIZATION OF ANODIC MATERIALS FOR LITHIUM-ION BATTERIES: THE CASE STUDY OF TiO<sub>2</sub>-RGO HYBRIDS FOR HIGH-POWER APPLICATIONS.

M. Minella<sup>1</sup>, C. Minero<sup>1</sup>, D. Versaci<sup>1</sup>, S. Casino<sup>2</sup>, F. Di Lupo<sup>2</sup>, S. Bodoardo<sup>2</sup>

<sup>1</sup>Department of Chemistry and NIS Inter-departmental Centre, University of Torino, via P. Giuria 5, Torino, 10125, Italy

<sup>2</sup>GAME Lab, Department of Applied Science and Technology, Politecnico di Torino, c.so Duca degli Abruzzi 24, 10129 Torino, Italy

16.00-16.20 **Coffee break**

Sessione Parallela: **Sensori e Biosensori1 (SENSO1)**

*Aula Magna (ed. H3)*

*(Presiede: Salvatore Daniele)*

16.20-16.40 **SENSO-1** ORGANIC BIOELECTRONICS: A PROMISING CHOICE FOR THE DEVELOPMENT OF THE NEXT GENERATION OF POC DEVICES

M. Magliulo, M.Y. Mulla, K. Manoli, D. De Tullio, P. Seshadri, A. Tiwari, G. Palazzo, L. Torsi

Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro" Via Orabona 4, 70126, Bari, Italy

16.40-17.00 **SENSO-2** SMARTPHONE-INTERFACED 3D PRINTED BIOSENSORS INTEGRATING BIOLUMINESCENT "SENTINEL CELL" FOR TOXICITY TESTING

L. Cevenini<sup>1</sup>, E. Michelini<sup>1,2</sup>, M.M. Calabretta<sup>1</sup>, G. Tarantino<sup>1</sup>, A. Roda<sup>1,2</sup>

<sup>1</sup>Department of Chemistry "G. Ciamician", University of Bologna Via Selmi, 2, Bologna.

<sup>2</sup>INBB, Istituto Nazionale di Biostrutture e Biosistemi, Viale Medaglie d'Oro 305, Roma.

Sessione Parallela: **Ambiente e Green Chemistry 1 (AMBG1)**

*Aula 1A (ed. H3)*

*(Presiede: Andrea Tapparo)*

15.00-15.20 **AMBG-1** QuEChERS METHOD IN THE DETERMINATION OF POLY(HYDROXYALKANOATES) IN BACTERIA BY ANALYTICAL PYROLYSIS: TOWARD AN ON-LINE MONITORING OF BIOTECHNOLOGICAL PROCESSES

C.Torri<sup>1,2</sup>, C. Samorì<sup>2</sup>, F. Abbondanzi<sup>2</sup>, G. Carvalho<sup>3</sup>, D. Fabbri<sup>1,2</sup>

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<sup>2</sup>Centro Interdipartimentale di Ricerca Industriale Energia e Ambiente, Università di Bologna.

<sup>3</sup>Department of Chemistry, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa.

15.20-15.40 **AMBG-2** ANALYSIS OF ANTITHYROID DRUGS IN SURFACE WATER BY USING LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY

V. Pérez-Fernández<sup>1</sup>, S. Marchese<sup>1</sup>, A. Gentili<sup>1</sup>, M.A. García<sup>2</sup>, R. Curini<sup>1</sup>, F. Caretti<sup>1</sup>, D. Perret<sup>1</sup>.

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<sup>2</sup>Department of Analytical Chemistry, University of Alcalá, Ctra.Madrid-Barcelona, Km. 33.600, 28871, Alcalá de Henares (Madrid), Spain

15.40-16.00 **AMBG-3** ALTERNATIVE RENEWABLE BIOFUEL: CHARACTERIZATION OF VINE SHOOTS

M. Cantamessa, M. Ginepro, J. Tafur Marinos, V. Zelano

Dipartimento di Chimica, Università di Torino, Via P. Giuria, 7 - 10125 Torino

16.00-16.20 **Coffee break**

Sessione Parallela: **Scienza delle separazioni 2 (SEPA2)**

**Aula 1A (ed. H3)**

(*Presiede: Danilo Corradini*)

16.20-16.40 **SEPA-5** GRAPHENE-MODIFIED SILICA SORBENT FOR SOLID-PHASE EXTRACTION OF BENZOTRIAZOLES AND BENZOTHIAZOLES FROM WATER

A. Speltini, M. Sturini, F. Maraschi, L. Ferrari, A. Profumo

Dipartimento di Chimica, Università di Pavia, Via Taramelli, 12 – 27100 Pavia

16.40-17.00 **SEPA-6** OVERCOATED SOLID PHASE MICROEXTRACTION FIBER: A NEW APPROACH FOR DIRECT ANALYSIS IN RAW URINE SAMPLES

A. Naccarato<sup>1</sup>, E. Gionfriddo<sup>2</sup>, R. Elliani<sup>1</sup>, J. Pawliszyn<sup>2</sup>, G. Sindona<sup>1</sup>, A. Tagarelli<sup>1</sup>

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<sup>2</sup>Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, Canada N2L 3G1

Sessione Parallela: **Chimica Analitica Forense (FORE)**

**Aula 0B (ed. H3)**

(*Presiede: Marco Vincenti*)

14.50-15.20 **KN7** ANALYSIS OF NEW PSYCOACTIVE SUBSTANCES IN BIOLOGICAL MATRICES BY PLE FOLLOWED BY LC-MS/MS

M. Sergi

Facoltà di Bioscienze e Tecnologie Agroalimentari e Ambientali, Università di Teramo, Via C. Lerici, 1 – 64023 Mosciano S.A. (TE)

15.20-15.40 **FORE-1** ACCURATE MASS SCREENING WORKFLOWS FOR

## THE ANALYSIS OF NOVEL PSYCHOACTIVE SUBSTANCES

S. Fiorina<sup>1</sup>, A. Taylor<sup>2</sup>

<sup>1</sup>AB SCIEX Srl, Brugherio, MB, Italy

<sup>2</sup>AB SCIEX Inc, Concord, ON, Canada

15.40-16.00 **FORE-2** RECENT TRENDS IN THE ILLICIT CONSUMPTION OF *CANNABIS* DERIVATIVES: AN ANALYTICAL STUDY ON SEIZED MATERIALS

M. Protti<sup>1</sup>, R. Addobbati<sup>2</sup>, L. Micolini<sup>1</sup>, S. Girotti<sup>3</sup>, M. D'Elia<sup>4</sup>

<sup>1</sup>Laboratory of Pharmaco-Toxicological Analysis, Department of Pharmacy and Biotechnology, Alma Mater Studiorum – University of Bologna, Via Belmeloro, 6 – 40126 Bologna

<sup>2</sup>IRCCS Burlo Garofolo, Via dell'Istria, 65 – 34137 Trieste

<sup>3</sup>Laboratory of Analytical Chemistry, Department of Pharmacy and Biotechnology, Alma Mater Studiorum – University of Bologna, Via San Donato, 15 – 40127 Bologna

<sup>4</sup>Emilia Romagna Regional Bureau of Scientific Police, Via Volto Santo, 3 – 40123 Bologna

16.00-16.20 **Coffee break**

16.20-16.40 **FORE-3** COCAINE PROFILING: ATR-FTIR SPECTROSCOPY COUPLED TO CHEMOMETRICS AS A RAPID QUANTIFICATION TOOL

R. Risoluti<sup>1</sup>, S. Materazzi<sup>1</sup>, A. Apriceno<sup>1</sup>, A. Gregori<sup>2</sup>, L. Ripani<sup>2</sup>

<sup>1</sup>Dipartimento di Chimica, “Sapienza” Università di Roma, p.le A.Moro 5 – 00185 Roma

<sup>2</sup>Reparto Investigazioni Scientifiche RIS – viale Tor di Quinto 119 – 00191 Roma

16.40-17.00 **FORE-4** INNOVATIVE CHEMOMETRIC INTERPRETATION OF AN EXTENDED STEROIDAL MODULE IN THE ATHLETE BIOLOGICAL PASSPORT

E. Alladio<sup>1,2</sup>, R. Caruso<sup>2</sup>, E. Gerace<sup>2</sup>, A. Salomone<sup>2</sup>, M. Vincenti<sup>1,2</sup>

<sup>1</sup>Dipartimento di Chimica, Università degli Studi di Torino, via P. Giuria 7, 10125 Torino, Italy

<sup>2</sup>Centro Regionale Antidoping e di Tossicologia “A. Bertinaria”, Regione Gonzole 10/1, 10043 Orbassano (TO), Italy

17.00-18.00 **Assemblee dei Gruppi** Divisionali e Interdivisionali (Aule: Magna, 1A, 1C e 0B)

18.15-20.00 **Passeggiata Turistica** nel Centro di Trieste (ritrovo in piazza Unità d'Italia, presso la fontana davanti al Municipio)

Alle 21.00 **Cena tipica** Triestino-Austriaca in Birreria (Birreria Spiller, *Riva Nazario Sauro, 14*)

# Mercoledì 16 Settembre 2015

## Sessione Plenaria

*Aula Magna (ed. H3)*

Conferenza Plenaria (*Presiede: Rosanna Toniolo*)

- 9.00-9.45 **PL3 CHALLENGES TO DETECT AND QUANTIFY OF NANOMATERIALS IN CONSUMER PRODUCTS**  
E. Anklam  
European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, 2440 Geel, Belgium

## Sessione Parallela: **Alimenti e Nutraceutici (ALI)**

*Aula Magna (ed. H3)*

(*Presiede: Aldo Laganà*)

- 10.10-10.30 **ALI-1 APPLICATION OF 3-WAY PRINCIPAL COMPONENT ANALYSIS FOR EVALUATING YOGURT STABILITY**  
M. Casale<sup>1</sup>, L. Bagnasco<sup>1</sup>, B. Aliakbarian<sup>2</sup>, P. Perego<sup>2</sup>, S. Lanteri<sup>1</sup>, R. Leardi<sup>1</sup>  
<sup>1</sup>Dipartimento di Farmacia, Università di Genova, Via Brigata Salerno 13, I-16147 Genova  
<sup>2</sup>Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova, Via Opera Pia 15, I-16145 Genova.
- 10.30-10.50 **ALI-2 SIMULTANEOUS ANALYSIS OF INTACT GLUCOSINOLATES AND CORRESPONDING ISOTHIOCYANATES BY LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY IN STARTING BIOMASSES AND ENRICHED BAKERY PRODUCTS.**  
P. Franco<sup>1</sup>, S. Spinozzi<sup>1</sup>, E. Pagnotta<sup>2</sup>, L. Lazzeri<sup>2</sup>, L. Ugolini<sup>2</sup>, C. Camborata<sup>1</sup>, A. Roda<sup>1</sup>  
<sup>1</sup>Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via Selmi, 2 – 40126 Bologna  
<sup>2</sup>Centro di Ricerca per le Colture Industriali (CRA-CIN), Via di Corticella, 133 – 40128 Bologna
- 10.50-11.10 **ALI-3 COMPARISON BETWEEN BERBERINE AND BERBERRUBINE BIODISTRIBUTION AFTER ORAL ADMINISTRATION IN RATS BY HPLC-ES-MS/MS**  
S. Spinozzi<sup>1</sup>, C. Camborata<sup>1</sup>, R. Aldini<sup>2</sup>, C. Caliceti<sup>1</sup>, F. Neri<sup>3</sup>, L. Maroni<sup>3</sup>, M. Roberti<sup>2</sup>, A. Roda<sup>1</sup>  
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<sup>2</sup>Dipartimento di Farmacia e Biotecnologie, Università di Bologna, Via Belmeloro 6, 40126 Bologna  
<sup>3</sup>Dipartimento di Scienze Mediche e Chirurgiche, Università di Bologna, Via Massarenti 9, 40138

11.10-11.40 **Coffee break**

(*Presiede: Chiara Cavaliere*)

11.40-12.00 **ALI-4** COUPLING OF HIGH TEMPERATURE LIQUID CHROMATOGRAPHY TO ICPMS FOR THE DETERMINATION OF ARSENIC AND SELENIUM SPECIES RELEVANT FOR FOOD SAFETY ASSESSMENT

A. Terol, F. Ardini, M. Grotti

Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso, 31 – 16146 Genova, Italy.

12.00-12.20 **ALI-5** SYNTHESIS AND CHARACTERISATION OF MODEL Ag/polymer SYSTEMS FOR THE ASSESSMENT OF SILVER RELEASE FROM ANTIBACTERIAL PACKAGING

S. Recchia<sup>1</sup>, M. Marelli<sup>2</sup>, C. Dossi<sup>3</sup>, D. Monticelli<sup>1</sup>.

<sup>1</sup>Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, via Valleggio 11 – 22100 Como.

<sup>2</sup>CNR-ISTM via C. Golgi 19 – 20133 Milano.

<sup>3</sup>Dipartimento di Scienze Teoriche e Applicate, Università degli Studi dell'Insubria, via Dunant 3 – 21100 Varese.

12.20-12.40 **ALI-6** USE OF A LC-DAD-QTOF SYSTEM FOR THE IDENTIFICATION OF MARKER COMPOUNDS IN ARGENTINEAN *ZUCCAGNIA PUNCTATA* AND RELATED PROPOLIS

E. Solorzano<sup>1,2</sup>, C. Bortolini<sup>1</sup>, S. Bogialli<sup>1</sup>, P. Pastore<sup>1</sup>

<sup>1</sup>Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo, 1 – 35131 Padova

<sup>2</sup>Permanent address: INQUINOA (Instituto de Química del Noroeste Argentino-CONICET) presso Instituto de Química Física, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, San Lorenzo 456 – T4000CAN, S. M. de Tucumán, Argentina

12.40-13.00 **ALI-7** PEDOT MODIFIED ELECTRODES FOR THE DETERMINATION OF COLOUR INDEX AND POLYPHENOL CONTENT IN WINES

L. Pigani, C. Rioli, R. Seeber, C. Zanardi, B. Zanfognini

Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia, via G. Campi 103, 41125 Modena

Sessione Parallela: **Sensori e Biosensori 2 (SENSO2)**

**Aula 1A (ed. H3)**

(*Presiede: Renato Seeber*)

10.00-10.30 **KN8** ELECTROCATALYTIC COATINGS IN AMPEROMETRIC SENSING: ADVANTAGES AND CRITICISMS

C. Zanardi, L. Pigani, F. Terzi, B. Zanfognini, R. Seeber

Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, via G. Campi 103, 41125 Modena

10.30-10.50 **SENSO-3** LABEL AND LABEL-FREE ELECTROCHEMICAL



## BIOSENSING PLATFORMS FOR microRNA DETECTION

D. Voccia, F. Bettazzi, I. Palchetti

Dipartimento di Chimica "Ugo Schiff", Università degli studi di Firenze, Via della Lastruccia 3 - 50019, Sesto Fiorentino

- 10.50-11.10 **SENSO-4** BIOSENSORS FOR PESTICIDES DETECTION: AN INNOVATIVE ELECTROCHEMICAL DNA-BASED SENSOR FOR ACETAMIPRID

R. Rapini, G. Marrazza

Dipartimento di Chimica "Ugo Schiff", Università degli studi di Firenze, via della Lastruccia, 3 – 50019 Sesto Fiorentino (FI)

- 11.10-11.40 **Coffee break**

- 11.40-12.00 **SENSO-5** ULTRASENSITIVE DETECTION OF MULTIPLE GENETIC LEUKEMIA BIOMARKERS BY MEANS OF SURFACE ENHANCED RAMAN SPECTROSCOPY

C. Morasso<sup>1</sup>, S. Picciolini<sup>1</sup>, D. Mehn<sup>1</sup>, R. Vanna<sup>1</sup>, A. Gualerzi<sup>1</sup>, P. Pellacani<sup>2</sup>, G. Marchesini<sup>2</sup>, F. Ciceri<sup>3</sup>, F. Gramatica<sup>1</sup>

<sup>1</sup>Labion - Laboratory of Nanomedicine and Clinical Biophotonics, Fondazione Don Carlo Gnocchi ONLUS, Via Capecelatro 66, 20148 Milano

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<sup>3</sup>IRCCS Ospedale San Raffaele, Via Olgettina 60, 20132 Milano

- 12.00-12.20 **SENSO-6** AFFINITY SENSOR FOR 2-FURFURAL BASED ON SYNTHETIC RECOGNITION ELEMENTS AND ELECTROCHEMICAL TRANSDUCTION AT SCREEN PRINTED CELL

M. Pesavento<sup>1</sup>, D. Merli<sup>1</sup>, A. Speltini<sup>1</sup>, G. Alberti<sup>1</sup>, R. Biesuz<sup>1</sup>, N. Cennamo<sup>2</sup>

<sup>1</sup>Dipartimento di Chimica, Università di Pavia, Via Taramelli, 12 – 27100 Pavia

<sup>2</sup>Dipartimento di Ingegneria Industriale e Informatica, Seconda Università di Napoli, Via Roma, 29 – 81031 Aversa

- 12.20-12.40 **SENSO-7** PLATINUM NANOSPHERES AND NANOFLOWERS MODIFIED ELECTRODES FOR DIRECT ELECTRON TRANSFER OF LACCASE FROM *TRAMETES VERSICOLOR*

G. Sanzón<sup>1,2</sup>, I. Taurino<sup>2</sup>, G. De Micheli<sup>2</sup>, S. Carrara<sup>2</sup>, G. Favero<sup>1</sup>, F. Mazzei<sup>1</sup>

<sup>1</sup>Dipartimento di Chimica e Tecnologia del Farmaco, "Sapienza" Università di Roma, Piazzale Aldo Moro, 5 – 00185 Roma

<sup>2</sup>Laboratory of Integrated Systems, École Polytechnique Fédérale de Lausanne, Station 14/EPFL, 1015 Lausanne Switzerland

- 12.40-13.00 **SENSO-8** ALL-IN-PAPER ELECTROCHEMICAL SENSOR TO DETECT PHOSPHATES

S. Cinti, D. Talarico, F. Arduini, G. Palleschi, D. Moscone

Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", Via della Ricerca Scientifica, 1 – 00133 Roma

Sessione Parallela: **Ambiente e Green Chem. 2 (AMBG2)**

**Aula 0B (ed. H3)**

(*Presiede: Claudio Minero*)

- 10.10-10.30 **AMBG-4** ICP-MS-BASED ISOTOPIC ANALYSIS OF ENVIRONMENTAL SAMPLES COLLECTED FROM POLAR REGIONS  
M. Grotti<sup>1</sup>, A. Bazzano<sup>1</sup>, F. Ardini<sup>1</sup>, K. Latruwe<sup>2</sup>, F. Vanhaecke<sup>2</sup>  
<sup>1</sup>Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso, 31 – 16146 Genova, Italy.  
<sup>2</sup>Department of Analytical Chemistry, Ghent University, Krijgslaan, 281-S12 – 9000 Ghent, Belgium.
- 10.30-10.50 **AMBG-5** PASSIVE SAMPLING AND STIR BAR SORPTIVE EXTRACTION: TWO INNOVATIVE APPROACHES FOR THE DETERMINATION OF NONSTEROIDAL ANTI-INFLAMMATORY DRUGS AND OTHER POLAR CONTAMINANTS IN WATER  
E. Magi, M. Di Carro, S. Tanwar, F. Ardini  
Dipartimento Chimica e Chimica Industriale, Università di Genova, via Dodecaneso, 31 – 16147 Genova
- 10.50-11.10 **AMBG-6** HINTS ON PAST SEA ICE CHANGES AND SOLAR ACTIVITY FROM TALOS DOME SITE (EAST ANTARCTICA)  
R. Traversi, S. Becagli, L. Caiazzo, D. Frosini, M. Severi and R. Udisti  
Dipartimento di Chimica “U.Schiff”, Università degli Studi di Firenze, Via della Lastruccia, 3, I -50019 Sesto F.no (Firenze).
- 11.10-11.40 **Coffee break**
- 11.40-12.00 **AMBG-7** SOURCES, TRANSPORT PROCESSES AND CLIMATIC IMPACT OF POLAR AEROSOL. A MULTI-YEAR ITALIAN EXPERIENCE.  
R. Udisti, on behalf of the Italian Aerosol Research Group.  
Dept. of Chemistry, Univ. of Florence, 50019 Sesto F.no (FI), Italy.
- 12.00-12.20 **AMBG-8** PYROLYSIS AND GASIFICATION OF WOODSTOCKS: ANALYSIS OF ORGANIC COMPOUNDS  
M. Cantamessa, M. Ginepro, J. Tafur Marinos, V. Zelano  
Dipartimento di Chimica, Università di Torino, Via P. Giuria, 7 - 10125 Torino
- 12.20-12.40 **AMBG-9** SYSTEMIC INSECTICIDES FROM CORN COATED SEEDS. A LC-HRMS STUDY ON METHIOCARB AND ITS METABOLITES IN GUTTATION DROPS  
A. Lentola<sup>1</sup>, S. Bogialli<sup>1</sup>, V. Girolami<sup>2</sup>, A. Tapparo<sup>1</sup>  
<sup>1</sup>Dipartimento di Scienze Chimiche, Università degli Studi di Padova, via Marzolo 1 - 35131 Padova  
<sup>2</sup>Dipartimento di Agronomia Animali Alimenti Risorse Naturali e Ambiente, Università degli Studi di Padova, Agripolis, viale Università 16 - 35020 Legnaro, Padova
- 12.40-13.00 **AMBG-10** ANALYTICAL METHODS WITH MINIMAL SAMPLE PRETREATMENT FOR THE CHARACTERISATION

## OF TRACE COMPOUNDS IN BIOCHAR

D. Fabbri<sup>1,2</sup>, M. Ghidotti<sup>1,2</sup>, M. Montalti<sup>2</sup>, J. Manzi<sup>2</sup>, A. Hornung<sup>3</sup>

<sup>1</sup>CIRI Energia e Ambiente, Università di Bologna, Campus di Ravenna, via S. Alberto 163, I-48123 Ravenna;

<sup>2</sup>Dipartimento di Chimica G.Ciamician, Università di Bologna, via Selmi 2, Bologna;

<sup>3</sup>Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT, Institute Branch Sulzbach-Rosenberg (Germany)

13.00-14.00 **Pranzo** (*edificio I*)

14.00-15.00 **SESSIONE POSTER P3: P107-P161 (AMBG-BIO-TOSS)**

Sessione Parallela: **Bioanalitica e Omics1 (BIO1)**

**Aula Magna (ed. H3)**

(*Presiede: Mara Mirasoli*)

15.00-15.30 **KN9 CHALLENGES IN FOOD PROTEOMICS FOR THE SELECTION OF LOW TOXICITY WHEAT GENOTYPES TOWARDS CELIAC DISEASE PATIENTS**

R. Pilolli, L. Monaci

Istituto di Scienze delle Produzioni Alimentari, ISPA-CNR, via G. Amendola 122/O, 70126, Bari

15.30-15.50 **BIO-1 RATIONAL DESIGN OF pH-CONTROLLED DNA STRAND DISPLACEMENT**

A. Amodio<sup>1,2</sup>, A. Porchetta<sup>2</sup>, A. Idili<sup>2</sup>, M. Castronovo<sup>1</sup>, F. Ricci<sup>2</sup>

<sup>1</sup>School of Nanotechnology, Department of Physics, University of Trieste, Via Valerio 2 - 34127 Trieste

<sup>2</sup>Dipartimento di Scienze e Tecnologie Chimiche, University of Rome, Tor Vergata, Via della Ricerca Scientifica, 1 - 00133 Rome

15.50-16.10 **BIO-2 POST-TRANSLATIONAL MODIFICATIONS: DEVELOPMENT OF NEW MATERIALS FOR THE ENRICHMENT OF PHOSHOPEPTIDES**

S. Piovesana, A.L. Capriotti, F. Ferraris, R. Samperi, A. Laganà

Dipartimento di Chimica, Università di Roma "La Sapienza", Piazzale A. Moro, 5 - 00185 Roma

16.10-16.30 **BIO-3 A FLUORESCENT IMMUNOCHROMATOGRAPHIC STRIP TEST USING QUANTUM DOTS FOR FUMONISINS DETECTION**

F. Di Nardo<sup>1</sup>, L. Anfossi<sup>1</sup>, C. Giovannoli<sup>1</sup>, C. Passini<sup>1</sup>, I. Y. Goryacheva<sup>2</sup>, E. S. Speranskaya<sup>2</sup> and C. Baggiani<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Turin, Via Giuria, 5 - 10125 Turin

<sup>2</sup>Department of Chemistry, Saratov State University, Astrakhanskaya, 83 - 410012 Saratov (Russia)

Sessione Parallela: **Sensori e Biosensori3 (SENSO3)**

**Aula 1A (ed. H3)**

(*Presiede: Giovanna Marrazza*)

- 15.00-15.30 **KN10 NATURE-INSPIRED DNA-BASED SENSORS**  
A. Porchetta, A. Idili, A. Amodio, S. Ranallo, E. Del Grosso, G. Palleschi, F. Ricci  
Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma, Tor Vergata, 00133 Roma
- 15.30-15.50 **SENSO-9 DEVELOPMENT AND COMPARISON OF ELIME ASSAY AND REAL-TIME PCR FOR DETECTING OF SALMONELLA IN IRRIGATION WATERS**  
L. Fabiani<sup>1</sup>, G. Volpe<sup>1</sup>, E. Delibato<sup>2</sup>, E. Pucci<sup>2</sup>, S. Piermarini<sup>1</sup>, F. Capuano<sup>3</sup>, G. Palleschi<sup>1</sup>  
<sup>1</sup>Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma Tor Vergata, via della Ricerca Scientifica 1 e-mail [laura.fabiani@uniroma2.it](mailto:laura.fabiani@uniroma2.it)  
<sup>2</sup>Dipartimento di Sanità Pubblica Veterinaria e Sicurezza Alimentare, Istituto Superiore di Sanità, viale Regina Elena 299, Roma  
<sup>3</sup>Dipartimento Ispezione Alimenti, Istituto Zooprofilattico Sperimentale del Mezzogiorno, via della Salute 2, Portici (NA)
- 15.50-16.10 **SENSO-10 DESIGN, FABRICATION AND CHARACTERIZATION OF ULTRA-SENSITIVE FLOW-THROUGH OPTOFLUIDIC MICRORESONATOR FOR (BIO)SENSING APPLICATIONS**  
E. Mazzotta<sup>1</sup>, A. Turco<sup>1</sup>, C. Malitesta<sup>1</sup>, L.M. Strambini<sup>2</sup>, S. Mariani<sup>2</sup>, G. Barillaro<sup>2</sup>, S. Berneschi<sup>3</sup>, A. Giannetti<sup>3</sup>, G.N. Conti<sup>3</sup>, F. Baldini<sup>3</sup>, G. Testa<sup>4</sup>, R. Bernini<sup>4</sup>, L. Tedeschi<sup>5</sup>, C. Domenici<sup>5</sup>  
<sup>1</sup>Dipartimento di Scienze e Tecnologie Biologiche e Ambientali (Di.S.Te.B.A.), Università del Salento, Lecce  
<sup>2</sup>Dipartimento di Ingegneria dell'Informazione, Università di Pisa, Pisa  
<sup>3</sup>Istituto di Fisica Applicata "Nello Carrara", CNR, Sesto Fiorentino, Firenze  
<sup>4</sup>Istituto per il Rilevamento Elettromagnetico dell'Ambiente, CNR, Napoli  
<sup>5</sup>Istituto di Fisiologia Clinica, CNR, Pisa
- 16.10-16.30 **SENSO-11 PEPTIDE BASED SENSING SYSTEMS FOR THE SELECTIVE DETECTION OF CHLOROGENIC ACID DERIVATIVES**  
D. Compagnone<sup>1</sup>, D. Capoferri<sup>1</sup>, M. Mascini<sup>1</sup>, F. Della Pelle<sup>1</sup>, M. Sergi<sup>1</sup>, M. Del Carlo<sup>1</sup>, C. Forzato<sup>2</sup>, F. Berti<sup>2</sup>  
<sup>1</sup>Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Via Lericci 1, 64023, Teramo, Italy  
<sup>2</sup>Department of Chemical and Pharmaceutical Sciences, University of Trieste, via Giorgieri 1 - 34127 TRIESTE

Sessione Parallela: **Tossicologia e salute Umana (TOSS)**

**Aula 0B (ed. H3)**

(*Presiede: Carlo Dossi*)

- 15.00-15.30 **KN11 CHELATION THERAPY IN METAL INTOXICATION**  
G. Crisponi, V.M. Nurchi  
Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari,  
Cittadella Universitaria, 09042 Monserrato-Cagliari
- 15.30-15.50 **TOSS-1 LABEL-FREE SURFACE-ENHANCED RAMAN SPECTROSCOPY OF BIOFLUIDS: DIAGNOSTIC APPLICATIONS IN ONCOLOGY**  
A. Bonifacio and V. Sergio  
Dip. di Ingegneria ed Architettura, Università di Trieste, P.le Europa, 1 – 34127 Trieste
- 15.50-16.10 **TOSS-2 THALLIUM CONCENTRATION LEVELS IN HAIR, URINE AND SALIVA IN A CONTAMINATED POPULATION IN THE NORTHWEST OF ITALY**  
E. Bramanti<sup>1</sup>, M. Onor<sup>1</sup>, B. Campanella<sup>1,2</sup>, A. D’Ulivo<sup>1</sup>, S. Biagi<sup>1</sup>, G. Rossi<sup>3</sup>, O. Curzio<sup>3</sup>, R. Giannecchini<sup>4</sup>, M. D’Orazio<sup>4</sup>, R. Petri<sup>4</sup>  
<sup>1</sup>C.N.R Institute of Chemistry of Organometallic Compounds, UOS of Pisa, via Moruzzi 1, 56124 Pisa, Italy  
<sup>2</sup>University of Pisa, Department of Chemistry and Industrial Chemistry, via Moruzzi 3, 56124 Pisa, Italy  
<sup>3</sup>C.N.R Istituto di Fisiologia Clinica, via Moruzzi 1, 56124 Pisa, Italy  
<sup>4</sup>University of Pisa, Department of Earth Sciences, via S. Maria, 56127 Pisa, Italy
- 16.10-16.30 **TOSS-3 SAMPLING AND CHARACTERIZATION OF MICRO- AND NANOPARTICLES FROM GAS TUNGSTEN ARC WELDING (GTAW) FUMES**  
C. Bianco<sup>1</sup>, E. Belluso<sup>2</sup>, E. Baracchini<sup>1</sup>, S. Capella<sup>2</sup>, V. Passini<sup>3</sup>, M. Crosera<sup>1</sup>, G. Adami<sup>1</sup>, F. Larese Filon<sup>4</sup>  
<sup>1</sup>Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via Giorgieri 1 - 34127 Trieste  
<sup>2</sup>Dipartimento di Scienze della Terra, Università di Torino, Via Valperga Caluso 35 - 10125 Torino  
<sup>3</sup>Laboratorio di Tossicologia ed Epidemiologia Industriale, CTO, Torino  
<sup>4</sup>UCO Medicina del Lavoro, Università di Trieste, Via della Pietà 19 – 34129 Trieste
- 16.30-17.00 **Trasferimento in centro Città**  
**Teatro Miela (Piazza Duca degli Abruzzi, 3)**
- 17.00-17.30 **Coffee break**

17.30-19.00 **Sessione Speciale:**

**INCONTRO PUBBLICO “ANALITICA@EXPO2015”**

**“Qualità e sicurezza alimentare: il SENSO della misura!”**

Intervengono:

**Paola Manini** - Autorità europea per la sicurezza alimentare (EFSA)

**Luciano Navarini** - Illycaffè SPA

**Claudio Mucchino** - Università degli Studi di Parma

**Federico Berti** - Università degli Studi di Trieste

Moderatore: **Cristina Serra**

Alle 20.30 **Cena di Gala**

*Hotel Savoia Excelsior Palace - Riva del Mandracchio 4*

*(Durante la serata: **premiazione dei migliori posters del congresso**)*

# Giovedì 17 Settembre 2015

## Sessione Plenaria

*Aula Magna (ed. H3)*

Conferenza Plenaria (*Presiede: Giuseppe Palleschi*)

9.00-9.45 **PL4** MEDIATED DNA SENSORS BASED ON SUPRAMOLECULAR AND ELECTROPOLYMERIZED CARRIERS

G. Evtugyn

Department of Analytical Chemistry of Chemistry Institute named after A.M.Butlerov, Kazan Federal University, 18 Kremlevskaya street, 420008, Kazan, Russian Federation

Sessione Parallela: **Bioanalitica e Omics2 (BIO2)**

*Aula Magna (ed. H3)*

(*Presiede: Aldo Roda*)

10.00-10.20 **BIO-4** THERMOCHEMILUMINESCENT REAGENTLESS ULTRASENSITIVE IMMUNOSENSOR USING ORGANICALLY MODIFIED SILICA NANOPARTICLES DOPED WITH NEW 1,2-DIOXETANE ANALOGUES AS LABELS IN A MINIATURIZED FORMAT

M. Di Fusco<sup>1,2</sup>, A. Quintavalla<sup>2</sup>, M. Lombardo<sup>2</sup>, M. Guardigli<sup>2</sup>, M. Mirasoli<sup>1,2</sup>, L. A. Andronico<sup>2</sup>, C. Trombini<sup>2</sup>, A. Roda<sup>2</sup>

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<sup>2</sup>Department of Chemistry “G. Ciamician”, Alma Mater Studiorum, University of Bologna, Via Francesco Selmi 2 – 40126 Bologna

10.20-10.40 **BIO-5** ICP-MS DETERMINATION OF THE METALLOME OF HUMAN PLACENTA IN GESTATIONAL DIABETES MELLITUS

M. Roverso<sup>1,2</sup>, C. Berté<sup>1</sup>, V. Di Marco<sup>1</sup>, D. Badocco<sup>1</sup>, P. Pastore<sup>1</sup>, S. Visentin<sup>3</sup>

<sup>1</sup>Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1 – 35131 Padova

<sup>2</sup>Dipartimento di Medicina, Università di Padova, via Giustiniani 2 – 35128 Padova

<sup>3</sup>Dipartimento di Salute della Donna e del Bambino, Università di Padova, via Giustiniani 2 – 35128 Padova

10.40-11.00 **BIO-6** LARGE AND FAST QUANTITATION OF PROTEINS WITH SWATH-MS IN A KNOCKDOWN CELL LINE

M. Manfredi<sup>1,2</sup>, S. Martinotti<sup>2</sup>, S. Biffo<sup>3</sup>, E. Mazzucco<sup>2</sup>, F. Gosetti<sup>2</sup>, E. Ranzato<sup>2</sup>, E. Marengo<sup>2</sup>

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<sup>2</sup>Università del Piemonte Orientale, Dipartimento di Scienze e Innovazione Tecnologica, viale T. Michel 11, 15121 Alessandria, Italy.

<sup>3</sup>INGM Istituto Nazionale Genetica Molecolare, Padiglione ROMEO INVERNIZZI ed ENRICA PESSINA - IRCCS Ospedale Maggiore Policlinico, Via Francesco Sforza 35, 20122 Milano, Italy

- 11.00-11.30 **Coffee break**
- 11.30-11.50 **BIO-7 NEEDLE TRAP MICRO-EXTRACTION: A NEW STRATEGY FOR THE COLLECTION AND PRE-CONCENTRATION OF BREATH SAMPLES**  
F. Di Francesco<sup>1</sup>, T. Lomonaco<sup>1</sup>, S. Ghimenti<sup>1</sup>, D. Biagini<sup>1</sup>, F.G. Bellagambi<sup>1</sup>, M. Onor<sup>2</sup>, R. Fuoco<sup>1</sup>  
<sup>1</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via G. Moruzzi, 13 – 56124 Pisa  
<sup>2</sup>Istituto di Chimica dei Composti Organometallici, Consiglio Nazionale delle Ricerche, Via G. Moruzzi, 1 – 56124 Pisa
- 11.50-12.10 **BIO-8 FUNCTIONALIZED TiO<sub>2</sub> NANOPARTICLES AS ENZYME-LIKE LABELS FOR IMMUNOASSAY**  
M. Sarro<sup>1</sup>, L. Anfossi<sup>1</sup>, C. Baggiani<sup>1</sup>, P. Calza<sup>1</sup>, M. Cerruti<sup>2</sup>, C. Giovannoli<sup>1</sup>  
<sup>1</sup>Dipartimento di Chimica, Università di Torino, Via P. Giuria, 7, 10125 Torino, Italia  
<sup>2</sup> Materials Engineering, McGill University, 3610 University St., Montreal, QC H3A 0C5, Canada
- 12.10-12.30 **BIO-9 DYNAMICS OF SILVER NANOPARTICLES IN HUMAN SKIN *IN VIVO* STUDIED BY SYNCHROTRON RADIATION AND ICP-MS**  
M. Roman<sup>1,2</sup>, C. Rigo<sup>1</sup>, H. Castillo-Michel<sup>3</sup>, I. Munivrana<sup>4</sup>, V. Vindigni<sup>4</sup>, W.R.L. Cairns<sup>2</sup>  
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<sup>2</sup>Istituto per la Dinamica dei Processi Ambientali (IDPA-CNR), Dorsoduro 2137 - 30123 Venezia  
<sup>3</sup>European Synchrotron Radiation Facility (ESRF), 71 avenue des Martyrs - 38000 Grenoble  
<sup>4</sup>Centro Ustioni, Divisione di Chirurgia Plastica, Ospedale Universitario di Padova, Via Giustiniani 2 - 35128 Padova
- 12.30-12.50 **BIO-10 ULTRASENSITIVE LATERALFLOW IMMUNO-ASSAY WITH CHEMILUMINESCENT DETECTION: NEW MINIATURIZED AND SMARTPHONE-BASED DEVICE**  
M. Zangheri<sup>1</sup>, L. Cevenini<sup>1</sup>, M. Mirasoli<sup>1</sup>, L. Anfossi<sup>2</sup>, F. Di Nardo<sup>2</sup>, C. Baggiani<sup>2</sup>, P. Simoni<sup>3</sup>, A. Roda<sup>1</sup>  
<sup>1</sup>Dipartimento di Chimica "G.Ciamician", Università di Bologna, Via Selmi2-40126 Bologna  
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<sup>3</sup>Dipartimento di Medicina e Chirurgia, Università di Bologna, Via Massarenti 9 – 40138 Bologna



Sessione Parallela: **Ambiente3 (AMBG3)**

**Aula 1A (ed. H3)**

(*Presiede: Paolo Pastore*)

- 10.00-10.20 **AMBG-11** DISTRIBUTION OF Cd, Pb AND Cu BETWEEN DISSOLVED FRACTION, INORGANIC PARTICULATE AND PHYTOPLANKTON IN TERRA NOVA BAY (ROSS SEA, ANTARCTICA) DURING AUSTRAL SUMMER 2011-12  
C. Truzzi, S. Illuminati, A. Annibaldi, T. Romagnoli, M. Antonucci, G. Libani, G. Scarponi, C. Totti  
Department of Life and Environmental Sciences, Università Politecnica delle Marche, via Brezze Bianche 60131 Ancona
- 10.20-10.40 **AMBG-12** SURFACE CHEMICAL CHARACTERISATION OF ATMOSPHERIC PARTICLES OF DIFFERENT SIZE USING XPS.  
M.R. Guascito<sup>1,2</sup>, D. Cesari<sup>2</sup>, D. Chirizzi<sup>3</sup>, D. Contini<sup>2</sup>  
<sup>1</sup>Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, 73100 Lecce, Italy.  
<sup>2</sup>Istituto di Scienze dell'Atmosfera e del Clima, ISAC-CNR, 73100 Lecce, Italy.  
<sup>3</sup>Dipartimento di Beni Culturali, Università del Salento, 73100 Lecce, Italy.
- 10.40-11.00 **AMBG-13** INDIVIDUAL PARTICLE SEM-EDX ANALYSIS: AN INTERESTING ANALYTICAL TOOL FOR PARTICULATE MATTER CHARACTERIZATION  
A. Genga<sup>1</sup>, M. Siciliano<sup>1</sup>, T. Siciliano<sup>2</sup>, C. Malitesta<sup>1</sup>, D. Aiello<sup>3</sup>, C. Tortorella<sup>3</sup>  
<sup>1</sup>Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Lecce, 73100, Italy  
<sup>2</sup>Dipartimento di Beni Culturali, Università del Salento, Università del Salento, Lecce, 73100, Italy  
<sup>3</sup>Enel Ingegneria e Ricerca – Ricerca e Innovazione - Litoranea S.na Brindisi Casalabate - Località Cerano - Tutturano (BR), Italy.
- 11.00-11.30 **Coffee break**
- 11.30-11.50 **AMBG-14** PARTICULATE MATTER AND DECAY OF MATERIALS: DEVELOPMENT OF A METHOD FOR SEM/EDS ANALYSIS OF ATMOSPHERIC DEPOSITION SAMPLED THROUGH “DEPOSITION BOX”  
L. Nobili<sup>1</sup>, E. Bernardi<sup>1</sup>, I. Vassura<sup>1</sup>, S. Raffo<sup>1</sup>, M. Casati<sup>2</sup>, L. Ferrero<sup>2</sup>, G. Sangiorgi<sup>2</sup>, G. Perrone<sup>2</sup>, E. Bolzacchini<sup>2</sup>  
<sup>1</sup>Dipartimento di Chimica Industriale “Toso Montanari”, Università di Bologna, Viale del Risorgimento, 4 – 40136 Bologna  
<sup>2</sup>Dipartimento di Scienze dell’Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano Bicocca, Piazza della Scienza, 1 – 20126 Milano
- 11.50-12.10 **AMBG-15** COMPETITIVE ADSORPTION OF ORGANIC POLLUTANTS AND LIGNIN DERIVATIVES PHENOLIC COMPOUNDS ON HYDROPHOBIC ZEOLITES  
E. Sarti<sup>1</sup>, L. Pasti<sup>1</sup>, A. Martucci<sup>2</sup>, R. Bagatin<sup>3</sup>, A. Cavazzini<sup>1</sup>  
<sup>1</sup>Department of Chemistry and Pharmaceutical Sciences, University of Ferrara,

via Fossato di Mortara 17, Ferrara

<sup>2</sup>Department of Physics and Earth Sciences, University of Ferrara, via Saragat 1, Ferrara

<sup>3</sup>Research Center for Non-Conventional Energy, Istituto Eni Donegani, Environmental Technologies, Via Maritano 26, San Donato Milanese (MI)

12.10-12.30 **AMBG-16 THE IMPACT OF SHIP TRAFFIC AND HARBOUR ACTIVITIES ON AIR QUALITY: THE CASE OF VENICE**  
E. Gregoris<sup>1,2</sup>, E. Barbaro<sup>1,2</sup>, A. Gambaro<sup>1,2</sup>, D. Contini<sup>3</sup>

<sup>1</sup>Dipartimento di Scienze Ambientali Informatica e Statistica, Università Ca' Foscari di Venezia, Dorsoduro, 2137 – 30123 Venezia

<sup>2</sup>Istituto per la Dinamica dei Processi Ambientali, Consiglio Nazionale delle Ricerche (IDPA-CNR), Dorsoduro, 2137 – 30123 Venezia

<sup>3</sup>Istituto di Scienze dell'Atmosfera e del Clima (ISAC-CNR) UOS di Lecce, Strada provinciale Lecce-Monteroni, km 1200 – 73100 Lecce

12.30-12.50 **AMBG-17 A FAST ROUTE TO THE DECONTAMINATION OF MICROWAVE VESSEL FROM CHLORINE SPECIES**

D. Monticelli<sup>1</sup>, C. Dossi<sup>2</sup>, S. Recchia<sup>1</sup>

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<sup>2</sup>Dipartimento di Scienze Teoriche e Applicate, Università degli Studi dell'Insubria, via Dunant 3 – 21100 Varese

***Aula Magna (ed. H3)***

12.50-13.00 **Chiusura del Congresso**

13.00-14.00 **Pranzo (*edificio I*)**

## **Sessione Poster 1 (Lunedì 14 Settembre 14.00-15.00)**

### **P01 USE OF LYSO-PHOSPHOLIPIDS AS MARKERS OF THERMAL TREATMENTS EFFECTED ON COMMERCIAL MUSSELS: A LC-ESI-MS STUDY**

L. Facchini<sup>1</sup>, I. Losito<sup>1,2</sup>, F. Palmisano<sup>1,2</sup>, T.R.I. Cataldi<sup>1,2</sup>

<sup>1</sup>Dipartimento di Chimica, <sup>2</sup>Centro di Ricerca Interdipartimentale S.M.A.R.T., Università degli Studi di Bari Aldo Moro, Via E. Orabona 4, 70126 Bari

### **P02 MULTIVARIATE CLASS MODELING TECHNIQUES APPLIED TO MULTIELEMENT ANALYSIS FOR THE AUTHENTICATION OF MEAT PRODUCTS OF “SUINO NERO DI CALABRIA”**

A. Naccarato, R. Elliani, E. Furia, G. Sindona, A. Tagarelli

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via Pietro Bucci, Cubo 12/C – 87036 Arcavacata di Rende (CS)

### **P03 NMR STUDY OF THE MICROWAVE-ASSISTED EXTRACTS OF AZADIRACHTA INDICA LEAVES**

S. Carradori<sup>1</sup>, A.P. Sobolev<sup>2</sup>, F. De Cosmi<sup>3</sup>, D. Secci<sup>3</sup>, A. Mollica<sup>1</sup>, M. Locatelli<sup>1</sup>, L. Mannina<sup>2,3</sup>

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<sup>2</sup>Institute of Chemical Methodologies, Magnetic Resonance Laboratory “Annalaura Segre”, National Research Council, Monterotondo, Rome, Italy.

<sup>3</sup>Department of Drug Chemistry and Technologies, Sapienza University of Rome, Rome, Italy.

### **P04 ASPHODELINE ROOTS AS A NEW SOURCE OF NATURAL COMPOUNDS: EVALUATION OF ANTIOXIDANTS, ENZYME INHIBITORS, AND CHEMICAL COMPOSITION.**

G. Zengin<sup>1</sup>, M. Locatelli<sup>2</sup>, L. Malatesta<sup>2</sup>, R. Ceylan<sup>1</sup>, A. Aktumsek<sup>1</sup>

<sup>1</sup>Selcuk University, Science Faculty, Department of Biology, Konya-Turkey

<sup>2</sup>University “G. d’Annunzio” Chieti-Pescara; Department of Pharmacy; via dei Vestini 31, 66100 Chieti; Italy.

### **P05 TARTARY BUCKWHEAT AS A SOURCE OF NUTRACEUTICALS: POLYPHENOL DETERMINATION BY PRESSURIZED LIQUID EXTRACTATION AND ULTRA HIGH PRESSURE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY**

R. Gatti\*, N. Ceriani, R. Caprioli

ENEA C.R. Casaccia, Technical Unit for Sustainable Development and Innovation of Agro-Industrial System, Via Anguillarese, 301 - 00123 Roma

### **P06 A NEW METHOD BASED ON A CORE-SHELL COLUMN FOR THE DETECTION OF SULPHONAMIDES IN MILK BY A CONVENTIONAL HPLC-DAD SYSTEM**

M. Muscarella<sup>1</sup>, A. Armentano<sup>1</sup>, S. Summa<sup>1</sup>, D. Nardiello<sup>2</sup>, C. Palermo<sup>2</sup>, D. Centonze<sup>2</sup>

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**P07 VALIDATION OF AN HPLC/FLD METHOD FOR AFLATOXIN B<sub>1</sub> DETECTION IN ANIMAL FEEDSTUFFS**

S. Lo Magro, A. Armentano, S. Summa, P. D'Antini, M. Muscarella  
Istituto Zooprofilattico Sperimentale di Puglia e Basilicata- Via Manfredonia, 20-71121 Foggia

**P08 FAST AND RELIABLE DETERMINATION OF PHTHALATES IN COFFEE**

M.V. Russo<sup>1</sup>, P. Avino<sup>2</sup>, G. Cinelli<sup>1</sup>

<sup>1</sup>Dipartimento Agricoltura, Ambiente e Alimenti, Università del Molise, via De Sanctis – 86100 Campobasso

<sup>2</sup>Dipartimento Innovazioni Tecnologiche, INAIL Area della Ricerca, via IV Novembre 144 – 00187 Roma

**P09 MICROARRAY ASSAY AS A SCREENING METHOD FOR THE DETERMINATION OF PROCESSED ANIMAL PROTEINS IN FEED**

L. Ambrosio, V. Brunetto, G. Molinari, A.F. Savino

Ministero Politiche Agricole Alimentari e Forestali – Dipartimento dell'Ispettorato Centrale della Tutela della Qualità e Repressione Frodi dei prodotti agroalimentari - Laboratorio di Salerno, Via Irno, 11 – 84135 Salerno

**P10 DETERMINATION OF YLOID IN SOIL ➔ OLIVE OIL FOOD CHAIN (OLEA EUROPEA) BY ICP-MS TECHNIQUE: A GEOGRAPHICAL CHARACTERIZATION OF FOOD PRODUCTS? A CASE STUDY. (III)**

L. Tutone, F. Saiano

Dipartimento di Scienze Agrarie e Forestali, Università di Palermo, Viale delle Scienze ed.4, – 90123 Palermo

**P11 LACTOFERRIN CONTENT AND TOTAL ANTIOXIDANT CAPACITY DETERMINATION IN FOOD INTEGRATORS, ANIMAL MILKS AND POWDERED MILK.**

M. Tomassetti, E. Martini, R. Angeloni, L. Campanella, G. Merola

Dipartimento di Chimica, "Sapienza" Università di Roma, piazzale Aldo Moro 5, 00185 Roma, Italia.

**P12 A NEW GC-FID METHOD FOR THE DETERMINATION OF MAIN SACCHARIDES IN MILK AND ITS APPLICATION TO VERIFY THE "LACTOSE FREE" CONDITION IN DIFFERENT DAIRY FOODSTUFFS**

I. Idda, N. Spano, M.I. Pilo, G. Sanna

Dipartimento di Chimica e Farmacia, Università di Sassari, Via Vienna, 2 – 07100 Sassari

**P13 PRELIMINARY RP-HPLC APPROACHES TO THE CHARACTERIZATION OF NUTRACEUTICAL COMPONENTS IN *STEVIA REBAUDIANA BERTONI*'S LEAVES**

N. Spano, M. Ciulu, M.I. Pilo, G. Sanna

Dipartimento di Chimica e Farmacia, Università di Sassari, Via Vienna, 2 – 07100 Sassari

**P14 VALIDATION OF A CONFIRMATORY METHOD FOR THE DETERMINATION OF QUINOLONES IN EGGS BY LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY**

L. Annunziata<sup>1</sup>, P. Visciano<sup>2</sup>, A. Stramenga<sup>1</sup>, M. Colagrande<sup>1</sup>, G. Campana<sup>1</sup>, G. Scortichini<sup>1</sup>, D. Compagnone<sup>2</sup>

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**P15 FTIR COUPLED WITH PLS-DA AGAINST FRAUDS: THE CASE OF HEAVY-SALTED DESALTED AND LIGHT-SALTED COD FILLETS**

M. De Rubeis, D. Pizzoni, D. Compagnone, M. Chiarini, A. Serio, A. Paparella  
Facoltà di Bioscienze e Tecnologie Agro-Alimentari e Ambientali, Università di Teramo, Via C.R. Lerici, 1 – 64023 Mosciano S.A (TE).

**P16 DETECTION OF COFFE POWDER ORIGIN BY ELECTRONIC NOSE AND GC-MS ANALYSIS**

D. Compagnone<sup>1</sup>, D. Mutarutwa<sup>1</sup>, D. Pizzoni<sup>1</sup>, P. Pittia<sup>1</sup>, L.Bucci<sup>1</sup>, L. Navarini<sup>2</sup>.

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**P17 INORGANIC COMPOSITION AND RAMAN SPECTROSCOPY AS NEW METHODS FOR THE IDENTIFICATION OF ANIMAL MEALS RESIDUED IN FEED.**

A. Giacomino<sup>1</sup>, L.M. Mercurio<sup>2</sup>, M. Malandrino<sup>2</sup>, O. Abollino<sup>2</sup>, L. Mandrile<sup>3</sup>, A.M. Rossi<sup>3</sup>, D. Marchis<sup>4</sup>.

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**P18 DETERMINATION OF OLIVE OIL ACIDITY: A NOVEL ELECTROANALYTICAL APPROACH**

M.A. Baldo<sup>1</sup>, P. Oliveri<sup>2</sup>, R. Simonetti<sup>2</sup>, S. Daniele<sup>1</sup>

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**P19 A NOVEL ANALYTICAL STRATEGY FOR THE ASSESSMENT OF TRACE HEAVY METAL CONTAMINATION IN OLIVE OILS**

M.A. Baldo<sup>1</sup>, M. Ongaro<sup>1</sup>, A.M. Stortini<sup>1</sup>, G. Cozzi<sup>2</sup>, M. Roman<sup>2</sup>, L.M. Moretto<sup>1</sup>, S. Daniele<sup>1</sup>, P. Ugo<sup>1</sup>

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<sup>2</sup>IDPA-CNR, Venezia S. Marta 2137 – 30123 Venezia

**P20 SPME-GC-qMS AND SPME-GCxGC-TFM-TOFMS CHARACTERIZATION OF VOLATILE COMPOUNDS OF AUTOCTONOUS WHITE WINES FROM THE COLLIO AREA**

A. Tolloi<sup>1</sup>, S.C. Briguglio<sup>1</sup>, E. Muzic<sup>1</sup>, L. Calamai<sup>2</sup>, F. Villanelli<sup>3</sup>, E. Sebastiani<sup>3</sup>, G. Adami<sup>1</sup>, P. Barbieri<sup>1,4</sup>

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<sup>4</sup>ARCo SolutionS srl, spin off del Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Piazzale Europa, 1 – 34127 Trieste

## **P21 SIMULTANEOUS DETERMINATION OF VITAMINS AND CAROTENES BY ON-LINE COLUMN FOCUSING FOLLOWED BY LIQUID CHROMATOGRAPHY AND UV DETECTION**

D. Nardiello<sup>1</sup>, C. Palermo<sup>1</sup>, M. Muscarella<sup>2</sup>, M. Quinto<sup>1</sup>, D. Li<sup>3</sup>, D. Centonze<sup>1</sup>

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## **P22 AEROSOL PARTICULATE MATTER STUDY FOR THE CONSERVATION OF URBAN MONUMENTAL HERITAGE: THE CASES OF FLORENCE AND MILAN**

P. Fermo<sup>1</sup>, A. Bonazza<sup>2</sup>, D. Gulotta<sup>3</sup>, L. Corbella<sup>1</sup>, L. Toniolo<sup>3</sup>

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<sup>3</sup>Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica, Via Mancinelli 7 – 20131 Milano

## **P23 A MULTITECHNIQUE APPROACH ON ANTONINIAN COINS FROM EGNATIA (SOUTHERN ITALY)**

L.C. Giannossa<sup>1</sup>, R. Gaudioso<sup>2</sup>, G. Giannelli<sup>1</sup>, A. De Giacomo<sup>1,2</sup>, R. Laviano<sup>3</sup>, A. Mangone<sup>1,4</sup>

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## **P24 PYROLYSIS-GC-MS OF MODERN INKS: THE FELT-TIP PENS USED BY LINA BO BARDI**

G. Germinario<sup>1</sup>, I.D. van der Werf<sup>1</sup>, A. Mirabile<sup>2</sup>, P. Moretti<sup>3</sup>, C. Miliani<sup>4,5</sup>, L. Sabbatini<sup>1,6</sup>

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Università degli Studi di Bari *Aldo Moro*, Bari

**P25 MULTIPLEXED CHEMILUMINESCENT LATERAL FLOW IMMUNOSENSOR FOR THE SIMULTANEOUS DETECTION OF OVALBUMIN AND COLLAGEN IN PAINT SAMPLES**

M. Zangheri<sup>1</sup>, G. Sciutto<sup>2</sup>, L. Anfossi<sup>3</sup>, S. Prati<sup>2</sup>, M. Mirasoli<sup>1</sup>, M. Guardigli<sup>1</sup>, F. Di Nardo<sup>3</sup>, C. Baggiani<sup>3</sup>, R. Mazzeo<sup>2</sup>, A. Roda<sup>1</sup>

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**P26 FURTHER STEPS TOWARDS THE CHARACTERIZATION OF THE ANCIENT *FOLIUM* DYE**

M. Aceto<sup>1</sup>, A. Arrais<sup>1</sup>, E. Calà<sup>1</sup>, C. Cassino<sup>1</sup>, M. Clericuzio<sup>1</sup>, F. Marsano<sup>1</sup>, A. Agostino<sup>2</sup>, G. Fenoglio<sup>2</sup>, M. Gulmini<sup>2</sup>, A. Idone<sup>2</sup>, L. Menghini<sup>3</sup>, L. Leporini<sup>3</sup>, N. Di Matteo<sup>3</sup>, C. Porter<sup>4</sup>

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**P27 DISCLOSING THE TECHNOLOGIES OF THE QING DYNASTY PAINTERS IN CIVIL BUILDINGS: THE MURAL PAINTINGS IN THE FIVE NORTHERN PROVINCES' ASSEMBLY HALL (ZIYANG, CHINA)**

A. Lluveras-Tenorio<sup>1</sup>, I. Bonaduce<sup>1</sup>, F. Sabatini<sup>1</sup>, I. Degano<sup>1</sup>, C. Blaensdorf<sup>2</sup>, E. Pouyet<sup>3</sup>, M. Cotte<sup>3,4</sup>, M. Linyan<sup>5</sup>, B. Chongbin<sup>4</sup>, H. Kejia<sup>6</sup>, M.P. Colombini<sup>1,7</sup>

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**P28 BEEKEEPING IN IRON AGE NORTHERN ITALY, A MULTI ANALYTICAL INVESTIGATION ON HONEYCOMB REMAINS FROM THE FORCELLO ETRUSCAN SITE**

F. Saliu<sup>1</sup>, L. Castellano<sup>2</sup>, I. Degano<sup>3</sup>, G. Furlanetto<sup>4</sup>, R. Pini<sup>4</sup>, C. Ravazzi<sup>4</sup>

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**P29 NEW INSIGHT ON THE DEVELOPMENT OF AN ENHANCED SENSITIVITY FTIR APPROACH FOR THE ANALYSES OF COLORANTS**

S. Prati<sup>1</sup>, M. Milosevic<sup>2</sup>, G. Sciuotto<sup>1</sup>, I. Bonacini<sup>1</sup>, S. Kazarian<sup>3</sup>, R. Mazzeo<sup>1</sup>

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**P30 DEVELOPMENT OF AN ELECTROCHEMICAL IMMUNOSENSOR FOR THE IDENTIFICATION OF EGG TEMPERA**

C. Gaetani, F. Bottari, P. Ugo, L.M. Moretto

Dipartimento di Scienze Molecolari e Nanosistemi, Università Cà Foscari Venezia, Calle Larga Santa Marta 2137 – 30123 Venezia

**P31 A FIRST INSIGHT AGAINST THE FALSIFICATION OF CLASSIC CARS: CHARACTERISATION OF STEEL FROM ALFA ROMEO MUSEUM VEHICLES**

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**P32 CHEMICAL ANALYSIS OF OPTICALLY DEGRADED DOCUMENTS OF THE TRIESTE CADASTRAL SYSTEM (1893): A SURPRISING IRON GALL INK PROTECTIVE ACTION**

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**P33 MULTIVARIATE RESOLUTION OF CARBONACEOUS RAMAN BROAD BANDS: A NOVEL APPROACH**

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**P34 AUTHENTICATION OF *BOLETUS EDULIS* AND ALLIED SPECIES BY NEAR INFRARED SPECTROSCOPY AND CHEMOMETRICS**

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**P35 ANCIENT STAMPS: REGUMMED OR NOT? A PATTERN RECOGNITION-SPECTROSCOPIC STUDY**

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**P36 BEER FINGERPRINTING AND MULTIVARIATE DATA ANALYSIS TOWARDS INFORMED TAILORED FOOD CONSUMPTION.**

N. Cavallini<sup>1,2</sup>, M. Cocchi<sup>1</sup>, R. Bro<sup>2</sup>, A. Biancolillo<sup>2,3</sup>, H. da Silva Friis<sup>2</sup>

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**P37 FROM HYPERSPECTRAL IMAGES TO SIGNALS: COMPARISON OF DIFFERENT DATA REDUCTION METHODS FOR FAST EXPLORATION AND CLASSIFICATION OF GREEN COFFEE SAMPLES**

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**P38 TRACEABILITY STUDY OF HAZELNUTS ALONG THE CHAIN OF PRODUCTION OF HAZELNUT PASTE IN A CONFECTIONERY BY THE DETERMINATION OF THE ELEMENTAL PROFILE BY ICP-MS AND MULTIVARIATE STATISTICAL METHODS**

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**P39 COUPLING OF NIR SPECTROSCOPY AND CHEMOMETRICS FOR THE AUTHENTICATION OF DRIED FRUITS**

S. De Luca, A. Furtivo, S. Bassi, R. Bucci, A.L. Magrì, A.D. Magrì, F. Marini

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**P40 N3 AND BNN: TWO NEW SIMILARITY BASED CLASSIFICATION METHODS IN COMPARISON WITH OTHER CLASSIFIERS**

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**P41 WEIGHTED REGULARIZED HASSE FOR CRITERIA WEIGHTING AND INCOMPARABILITY REDUCTION**

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**P42 IDENTIFICATION OF SULFORHODAMINE B PHOTO-DEGRADATION PRODUCTS PRESENT IN NON-PERMANENT TATTOOS BY MICRO LC-QTOF MS/MS**

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**P43 MAJOR SOYASAPONINS IN TRADITIONAL CULTIVARS OF FAGIOLI DI SARCONI BEANS INVESTIGATED BY LIQUID CHROMATOGRAPHY AND HIGH-RESOLUTION TANDEM MASS SPECTROMETRY**

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**P44 THE ENTIRE SUITE OF CARDIOLIPINS IN A BACTERIAL EXTRACT EXAMINED BY REVERSED-PHASE LIQUID CHROMATOGRAPHY WITH ELECTROSPRAY IONIZATION AND MULTISTAGE MASS SPECTROMETRY**

S. Granafei<sup>1</sup>, I. Losito<sup>1,2</sup>, M. Trotta<sup>3</sup>, F. Italiano<sup>2</sup>, V. De Leo<sup>1</sup>, F. Palmisano<sup>1,2</sup>, T.R.I. Cataldi<sup>1,2</sup>

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**P45 SILICON AND METAL-SILICON NANOWIRE ARRAYS FOR LASER DESORPTION IONIZATION MASS SPECTROMETRY APPLICATIONS**

R.A. Picca<sup>1</sup>, B. Fazio<sup>2</sup>, C.D. Calvano<sup>1</sup>, M.J. Lo Faro<sup>2</sup>, M.C. Sportelli<sup>1</sup>, C. D'Andrea<sup>3</sup>, A. Irrera<sup>2</sup>, N. Cioffi<sup>1</sup>

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**P46 SIMULTANEOUS DETERMINATION OF HALOGENATED CONTAMINANTS (PCBs AND PCNs) AND POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN BIOTA INTEGRATED INTO A SINGLE METHOD**

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**P47 A NEW APPROACH TO DETECT ANTIBIOTIC RESIDUES IN MUSCLE TISSUES: DEVELOPMENT OF A HIGH RESOLUTION MASS SPECTROMETRY SCREENING METHOD**

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**P48 ULTRA HIGH PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED TO HIGH RESOLUTION TANDEM MASS SPECTROMETRY: ACQUISITION STRATEGIES TO CHARACTERIZE COMPLEX PHYTOCHEMICAL MIXTURES. APPLICATION TO STRAWBERRY EXTRACT**

C. Cavaliere, A.L. Capriotti, G. La Barbera, S. Ventura, R. Samperi, A. Laganà

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**P49 DETERMINATION OF KNOWN/UNKNOWN IODINATED POLLUTANTS IN AQUATIC ECOSYSTEMS USING FULL-SCAN TANDEM MASS SPECTROMETRY TECHNIQUES**

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**P50 CHARACTERIZATION OF ADDUCTS BETWEEN CYCLODEXTRIN-CAPPED GOLD NANOPARTICLES AND BIOMOLECULES BY TAYLOR DISPERSION ANALYSIS AND CAPILLARY ELECTROPHORESIS**

V. Bosi<sup>1</sup>, E. Sarti<sup>1</sup>, L. Pasti<sup>1</sup>, G. Uccello-Barretta<sup>2</sup>, A. Cavazzini<sup>1</sup>

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**P51 INVESTIGATING THE FEASIBILITY OF COUPLING QuEChERS EXTRACTION, ON-LINE CLEAN-UP AND LC-MS/MS ANALYSIS OF EMERGENT MICROPOLLUTANTS IN SLUDGES**

M. Del Bubba<sup>1</sup>, D. Rossini<sup>1,2</sup>, L. Ciofi<sup>1</sup>, M.C. Bruzzoniti<sup>2</sup>

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**P52 EFFECT OF COSURFACTANT ON SEPARATION SELECTIVITY IN SOLVENT-MODIFIED MEKC: THE DICLOFENAC CASE**

C. Caprini<sup>1</sup>, F. Melani<sup>2</sup>, V. Fiordalisi<sup>2</sup>, S. Orlandini<sup>1</sup>, B. Pasquini<sup>1</sup>, R. Gotti<sup>3</sup>, S. Furlanetto<sup>1</sup>

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**P53 REDUCING THE PHTHALATES CONTAMINATION DURING THE ANALYSIS PROCESS USING GAS PURGE MICROSYPHINGE EXTRACTION.**

M. Quinto<sup>1</sup>, D. Centonze<sup>1</sup>, C. Palermo<sup>1</sup>, D. Nardiello<sup>1</sup>, G. Spadaccino<sup>1</sup>, D. Li<sup>2</sup>

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**P54 SUPRAMOLECULAR RECEPTORS IN SOLID PHASE FOR ANIONIC RADIONUCLIDES SEPERATION**

R. Biesuz, L. Bertuzzi, G. Alberti, G. Bergamaschi, A. Miljkovic, V. Amendola,  
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**P55 FLUORESCENT MESOPOROUS SILICA MATERIALS DISCRIMINATING Ag(I) AND Hg(II)**

R. Colleoni<sup>1</sup>, E. Climent<sup>2</sup>, K. Rurack<sup>2</sup>, R. Biesuz<sup>1</sup>.

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**P56 MULTICLASS DETERMINATION OF PESTICIDES IN WHEAT FLOUR BY MEPS FOLLOWED BY HPLC-MS/MS**

F. Di Ottavio<sup>1</sup>, F. Della Pelle<sup>1</sup>, C. Montesano<sup>2</sup>, M.C. Simenoni<sup>1</sup>, D. Compagnone<sup>1</sup>,  
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**P57 DIRECT INJECTION - HPLC ANALYSIS FOR THE DETERMINATION OF FURANIC COMPOUNDS IN OIL AS MARKERS OF SOLID INSULATION DEGRADATION IN POWER TRANSFORMERS**

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## **Sessione Poster 2 (Martedì 15 Settembre 14.00-15.00)**

### **P58 FORENSIC INVESTIGATION ON TEXTILES: CAPABILITIES OF RAMAN SPECTROSCOPY**

F. Bianchi<sup>1</sup>, V. Trola<sup>1</sup>, N. Riboni<sup>1</sup>, G. Avantaggiato<sup>2</sup>, G. Iacobellis<sup>2</sup>, G. Furlan<sup>2</sup>, M. Careri<sup>1</sup>

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### **P59 ANALYSIS OF DRUGS OF ABUSE: SYNTHETIC CANNABINOIDS AND ALL AROUNDERS**

D. Merli, S. Protti, M. Pesavento, S. Tinivella, L. Cucca, A. Profumo

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### **P60 LUMICYANO: EVALUATION OF A NEW FLUORESCENT CYANOACRYLATE IN FINGERMARKS DETECTION**

R. Risoluti<sup>1</sup>, S. Materazzi<sup>1</sup>, V. Filetti<sup>1</sup>, G. Iuliano<sup>2</sup>, L. Niola<sup>2</sup>, L. Ripani<sup>2</sup>

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### **P61 PRESSURIZED LIQUID EXTRACTION FOR THE DETERMINATION OF CANNABINOIDS AND METABOLITES IN HAIR: DETECTION OF CUT-OFF VALUES BY HPLC-HRMS/MS**

M. Sergi<sup>1</sup>, M.C. Simeoni<sup>1</sup>, G. Vannutelli<sup>2</sup>, C. Montesano<sup>2</sup>, A. Gregori<sup>3</sup>, L. Ripani<sup>3</sup>, D. Compagnone<sup>1</sup>, R. Curini<sup>2</sup>

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### **P62 DETERMINATION OF ANTICOAGULANT RODENTICIDES AND A-CHLORALOSE IN HUMAN HAIR BY ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY AND APPLICATION TO A REAL CASE**

A. Salomone<sup>1</sup>, M. Loporati<sup>1</sup>, G. Golè<sup>2</sup>, E. Gerace<sup>1</sup>, M. Vincenti<sup>1,3</sup>

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### **P63 THE NEVER ENDING STORY OF CANNABINOIDS IN HAIR**

D. Di Corcia<sup>1</sup>, F. Seganti<sup>1</sup>, E. Gerace<sup>1</sup>, A. Salomone<sup>1</sup>, M. Vincenti<sup>1,2</sup>

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### **P64 DETECTION OF 31 STIMULANT, PSYCHEDELIC AND DISSOCIATIVE DESIGNER DRUGS IN REAL HAIR SAMPLES**

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**P65 DIRECT DRUG TESTING IN ORAL FLUID BY TOUCH SPRAY-MASS SPECTROMETRY WITH MEDICAL SWABS**

V. Pirro<sup>1,2</sup>, A.K. Jarmusch<sup>1</sup>, M. Vincenti<sup>2,3</sup>, R.G. Cooks<sup>1</sup>

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**P66 ELECTRODEPOSITION OF P & N SEMICONDUCTOR LAYERS FOR PHOTOVOLTAIC APPLICATIONS**

E. Berretti<sup>1</sup>, S.Cinotti<sup>1</sup>, R.A. Picca<sup>2</sup>, F. Di Benedetto<sup>3</sup>, N. Cioffi<sup>2</sup>, A. De Luca<sup>1</sup>, A. Lavacchi<sup>4</sup> and M. Innocenti<sup>1</sup>

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**P67 ENANTIORECOGNITION TOWARDS L- AND D-DOPA ON EASY-TO-PREPARE INHERENTLY CHIRAL FILM ELECTRODES**

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**P68 TITANIUM AS AN ELECTRODE MATERIAL FOR AMPEROMETRIC SENSORS**

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**P69 ALKALINE PHOSPHATASE INHIBITION BASED BIOSENSOR FOR 2,4-DICHLOROPHENOXYACETIC ACID (2,4-D) DETECTION**

P. Bollella<sup>1</sup>, R. Antiochia<sup>1</sup>, C. Tortolini<sup>1,2</sup>, G. Sanzò<sup>1</sup>, G. Fusco<sup>1,2</sup>, G. Favero<sup>1</sup>, F. Mazzei<sup>1</sup>

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**P70 A NOVEL POLYPHENOL BIOSENSOR BASED ON GREEN ROOM TEMPERATURE IONIC LIQUID AND LACCASE FROM *TRAMETES VERSICOLOR***

P. Bollella<sup>2</sup>, R. Antiochia<sup>2</sup>, R. Caminiti<sup>1</sup>, C. Tortolini<sup>1,2</sup>, M.L. Antonelli<sup>1</sup>

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**P71 DIRECT EXPERIMENTAL DETERMINATION OF THE DELOCALIZED HOLE DOMAINS IN GUANINE-RICH DNA OLIGONUCLEOTIDES: A VOLTAMMETRIC APPROACH**

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**P72 ELECTRO-ANALYTICAL TRACE DETERMINATION OF ACETAMINOPHEN BY ANODIC ACTIVATION OF A GLASSY CARBON ELECTRODE (GCE)**

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**P73 EVALUATION OF AN ELECTROCHEMICAL ROOM TEMPERATURE IONIC LIQUID-BASED MICROPROBE FOR GAS ANALYSIS**

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**P74 ELECTRODEPOSITION OF Pt NANOPARTICLES ON POLYPYRROLE NANOWIRE NETWORK**

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**P75 ON THE INTERACTION OF RISEDRONIC ACID WITH MAJOR COMPONENTS OF BIO AND NATURAL FLUIDS**

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**P76 GLUCONIC ACID: THERMODYNAMIC PROPERTIES AND COMPLEXING ABILITY TOWARDS METAL CATIONS**

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**P77 INTERACTION OF N-ACETYL-L-CYSTEINE WITH DIVALENT METAL CATIONS**

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**P78 MODELLING OF PROTONATION CONSTANTS OF HALLOYSITE CLAY NANOTUBES IN VARIOUS AQUEOUS MEDIA, AT DIFFERENT IONIC STRENGTHS**

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**P79 Fe<sup>III</sup>, Al<sup>III</sup>, Cu<sup>II</sup> AND Zn<sup>II</sup> COMPLEX FORMATION STUDIES WITH BIS-KOJIC ACID DERIVATIVES.**

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**P80 KINETICS OF METAL ION ACCUMULATION ON THE RESIN CHELEX 100**

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**P81 GOLD MICROTUBES ASSEMBLING ARCHITECTURE FOR AN IMPEDIMETRIC GLUCOSE BIOSENSING SYSTEM**

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**P82 SMARTPHONE-BASED COLORIMETRIC ASSAY FOR CA125 CANCER BIOMARKER DETECTION**

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**P83 NOVEL APPROACHES FOR ALZHEIMER'S DISEASE BIOMOLECULAR DIAGNOSIS**

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**P84 DEVELOPMENT OF A SURFACE PLASMON RESONANCE BASED BIOSENSOR FOR OVALBUMIN DETECTION IN WINES**

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**P85 NANOPARTICLES MODIFIED SCREEN PRINTED ELECTRODE FOR ELECTROCHEMICAL DETERMINATION OF COD.**

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**P86 ETHANOL DETERMINATION IN WINE AND BEER USING A DIRECT CATALYTIC METHANOL FUEL CELL (DMFC)**

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**P87 STRUCTURE-SWITCHING DNA SENSORS BASED ON TRIPLE HELICES FORMATION**

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**P88 TESTING OF ALGAL TOXINS IN DRINKING, FRESH AND SEA WATER SAMPLES WITH AN OPTIMIZED COLORIMETRIC PHOSPHATASE INHIBITION ASSAY**

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**P89 ALLOSTERIC DNAZYME/RNAZYME FOR HIGH SPECIFIC DETECTION OF BIOLOGICAL AND ENVIRONMENTAL TARGET**

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**P90 A MULTI-APTASENSORS SYSTEM FOR THE DETECTION OF MARINE ALGAL TOXINS**

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**P91 CHITOSAN/CARBON BLACK NANOPARTICLES AS BIOCOMPATIBLE SCAFFOLD FOR ENZYME-BIOSENSORS DEVELOPMENT**

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#### **P92 CONTROLLING DNA-BASED REACTIONS AND NANODEVICES USING ENZYMATIC REACTIONS**

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#### **P93 ENSEMBLES OF GOLD NANOWIRES AS SENSORS FOR TRACE ARSENIC DETERMINATION IN WATER AND FOODSTUFF**

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#### **P94 NANOSTRUCTURED PRESS TRANSFERRED ELECTRODE COUPLED TO MICROFLUIDIC ELECTROPHORESIS, FOR PESTICIDE DETECTION**

F. Della Pelle<sup>1,2</sup>, M.C. González<sup>2</sup>, M. Sergi<sup>1</sup>, M. Del Carlo<sup>1</sup>, D. Compagnone<sup>1</sup>, A. Escarpa<sup>2</sup>

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#### **P95 SIMPLE PENCIL-DRAWN PAPER-BASED DEVICE FOR ONE-SPOT ELECTROCHEMICAL DETECTION OF ELECTROACTIVE SPECIES IN OIL SAMPLES**

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#### **P96 A DEEP EUTECTIC SOLVENT-BASED AMPEROMETRIC SENSOR FOR THE DETECTION OF LOW OXYGEN CONTENTS IN GASEOUS ATMOSPHERES**

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**P97** 5-PHENYL-DIPYRROMETHANE AND 5-(4-PYRIDYL)-DIPYRROMETHANE AS MODULAR BUILDING BLOCKS FOR BIO-INSPIRED CONDUCTIVE MOLECULARLY IMPRINTED POLYMER (cMIP).

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**P98** ELECTROCHEMICAL BIOSENSOR FOR THE DETECTION OF POLYBROMINATED DIPHENIL ETHERS (PBDEs) IN FOOD SAMPLES

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**P99** SYNTHESIS AND CHARACTERIZATION OF HYBRID Cu/Ag NANOPARTICLES BY LASER ABLATION IN LIQUID

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**P100** STUDY OF THE INTERACTION BETWEEN COLLAGEN AND NATURALIZED AND COMMERCIAL DYES VIA FOURIER TRANSFORM INFRARED SPECTROSCOPY

D. Pellegrini<sup>1</sup>, M. Corsi<sup>2</sup>, M. Bonanni<sup>2</sup>, R. Bianchini<sup>2</sup>, A. D'Ulivo<sup>1</sup>, E. Bramanti<sup>1</sup>

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**P101** PHOTOCHEMICAL VAPOR GENERATION OF SELENIUM(IV) AND ARSENIC(III) WITH COMMERCIAL AND HOMEMADE UV LAMPS

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**P102 IN VITRO SELECTION OF RNA APTAMER AGAINST CA125 TUMOR MARKER IN OVARIAN CANCER AND ITS STUDY BY OPTICAL BIOSENSING**

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**P103 DETERMINATION OF REY, Zr AND Hf IN HIGH ARSENIC CONTENT MATRIX. A CASE STUDY AT THE SOLFATARA OF PHLEGREAN FIELDS (NAPLES, ITALY)**

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**P104 XPS AND FTIR SPECTROSCOPY CHARACTERIZATION OF PHOTOTROPHIC BACTERIAL CELLS INTERACTING WITH NICKEL IONS**

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**P105 ANALYTICAL CHARACTERIZATION OF SILVER-NANOPARTICLE ANTIMICROBIAL COATINGS FOR FIORDILATTE CHEESE**

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**P106 XPS CHARACTERIZATION OF PDMS BASED MICROFLUIDIC CHANNELS OF CLINICAL APPLICATION TREATED WITH DIFFERENT SOLVENTS**

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### **Sessione Poster 3 (Mercoledì 16 Settembre 14.00-15.00)**

#### **P107 CONTAMINATION BY ORGANOTIN COMPOUNDS IN THE GULF OF LA SPEZIA AFTER THE INTERNATIONAL BAN OF TBT IN ANTIFOULING PAINTS**

P. Massanisso<sup>1</sup>, M. Pezza<sup>1</sup>, S. Cannarsa<sup>2</sup>, C. Cremisini<sup>1</sup>

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#### **P108 MAGNETIC AND HIGHLY REUSABLE MACROPOROUS SUPERHYDROPHOBIC/SUPEROLEOPHILIC PDMS/MWNTS NANOCOMPOSITE FOR OILS SORPTION FROM WATER**

A. Turco<sup>1</sup>, C. Malitesta<sup>1</sup>, G. Barillaro<sup>2</sup>, A. Greco<sup>3</sup>, A. Maffezzoli<sup>3</sup>, E. Mazzotta<sup>1</sup>

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#### **P109 QUANTIFICATION OF INDOLE-3-ACETIC ACID, BENZOIC ACID AND SALICYLIC ACID IN PLANT EXTRACTS BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY**

D. Ferraro<sup>1,2</sup>, M. Onor<sup>1</sup>, B. Campanella<sup>1,2</sup>, S. Tegli<sup>3</sup>, E. Bramanti<sup>1</sup>, A. D'Ulivo<sup>1</sup> and E. Pagliano<sup>4</sup>

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#### **P110 MONITORING OF MERCURY IN THE ITALIAN DOLOMITES.**

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#### **P111 ANALYSIS OF WC-Co NANOPARTICLES IN SLUDGE FROM A SEWAGE TREATMENT PLANT**

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**P112 ANALYSIS AND DETECTION OF DIURON IN SEAWATER BY PASSIVE SAMPLING**

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**P113 SPATIAL AND TEMPORAL VARIABILITY OF SNOW CHEMICAL COMPOSITION AND ACCUMULATION RATE AT TALOS DOME SITE (EAST ANTARCTICA)**

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**P114 SURFACE SNOW AT DOME C: CHEMICAL COMPOSITION FROM LONG-TERM CONTINUOUS RECORDS ON THE ANTARCTIC PLATEAU**

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**P115 FIVE YEARS OF AEROSOL SIZE DISTRIBUTION DURING SPRING-SUMMER CAMPAIGNS AT NY ÅLESUND (SVALBARD ISLANDS, NORWAY)**

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**P116 METALS AND LANTHANIDS DETERMINATION IN ATMOSPHERIC AEROSOL SAMPLES AS MARKERS OF HEAVY FUEL OIL PROCESSING SOURCES.**

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**P117 STUDY OF ATMOSPHERIC AEROSOL IN THE PROXIMITY OF A WASTE INCINERATOR PLANT IN TUSCANY**

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**P118 HIGH RESOLUTION FAST ION CHROMATOGRAPHY: RECOVERING PALEO-RECORDS FROM ANTARCTIC ICE-CORES.**

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**P119 DETERMINATION OF ALKYLPHENOLS IN RIVER WATER USING AN ETCHED STAINLESS STEEL WIRE - IONIC LIQUID - SOLID PHASE MICROEXTRACTION TECHNIQUE.**

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**P120 INFLUENCE OF ILLUMINATION ON LIPID COMPOSITION OF THE SOFT CORAL *Sinularia flexibilis***

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**P121 GLOBAL WARMING: INFLUENCE OF TEMPERATURE ON LIPID COMPOSITION OF ANTARCTIC FISH *Trematomus Bernacchii***

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**P122 DEEP CHEMICAL CHARACTERIZATION OF URBAN PARTICULATE MATTER**

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**P123 DEGRADATION STUDIES OF HERBICIDES USED IN RICE CULTIVATION**

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**P124 QUANTIFICATION AND SPECIATION OF COPPER IN PLANT TISSUES BY SIZE-EXCLUSION CHROMATOGRAPHY COUPLED WITH ICP-MS DETECTION**

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**P125 RAPID CLEAN-UP STRATEGY BASED ON MOLECULARLY IMPRINTED POLYMERS FOR THE DETERMINATION OF 3-INDOLEACETIC ACID IN PLANT EXTRACTS**

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**P126 ULTRA HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY ANALYSIS OF DIFFERENT CLASSES OF ENDOCRINE DISRUPTORS IN SEDIMENTS**

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**P127 IRON DISTRIBUTION IN LICHENS WITH DIFFERENT LEVELS OF MELANIZATION: A STUDY BY MEANS OF MICRO-XRF AND ICP-AES**

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**P128 BIOACCUMULATION OF TRACE METALS IN PLANTS GROWING NEARBY A DECOMMISSIONED Zn-Pb MINE (SALAFOSSA, NORTHEASTERN ITALIAN ALPS)**

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**P129 ORGANIC BIOMARKERS CHARACTERISATION IN PEAT SAMPLES**

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**P130 MELTING OF ANTARCTIC LAKES: SEASONAL INFLUENCE ON POPS AND AMINO ACIDS DYNAMICS**

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**P131 OCCURRENCE OF FRAGRANCES IN THE CANALS OF VENICE**

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**P132 COD AND TPH ANALYSIS IN SLOPS TREATMENT'S EXPERIMENTAL PLANTS: ANALYTICAL PROBLEMS.**

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**P133 HEAVY METALS AND PLATINUM GROUP METALS DETERMINATION IN OYSTERS, MUSSELS AND CLAMS AS BIOMONITORS OF POLLUTION IN THE ADRIATIC AQUATIC SYSTEM.**

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**P134 ANALYTICAL AND PREPARATIVE PYROLYSIS TO INVESTIGATE THE CONVERSION OF PROTEINACEOUS BIOMASS INTO HYDROCARBONS BY ZEOLITE CRACKING**

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**P135 ADSORPTION OF RARE EARTH IONS ONTO ZEOLITES**

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**P136 PHOTOCATALYTIC HYDROGEN GAS PRODUCTION FROM AQUEOUS CELLULOSIC BIOMASSES COUPLED WITH SOLID STORAGE BY INTERMETALLIC HYDRIDES AND METAL ORGANIC FRAMEWORKS: A PILOT STUDY**

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**P137 MONITORING THE STRESS RESPONSE OF ESCHERICHIA COLI TO NANOANTIMICROBIALS BY MALDI-TOF MASS SPECTROMETRY**

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**P138 PROTON-TRANSFER OR ELECTRON-TRANSFER MATRIX FOR MALDI TOF MS ANALYSIS OF CYCLIC TETRAPYRROLE DERIVATIVES**

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**P139 CHEMILUMINESCENT LATERAL FLOW IMMUNOASSAY FOR QUANTITATIVE DETECTION OF HUMAN SERUM ALBUMIN IN URINE EMPLOYING A CARTRIDGE WITH INTEGRATED AMORPHOUS SILICON PHOTODIODES**

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**P140 DETECTION OF VIRAL DNA BY ISOTHERMAL AMPLIFICATION AND CHEMILUMINESCENCE GENE PROBE HYBRIDIZATION ASSAY IN A SELF-STANDING MICROFLUIDIC CARTRIDGE**

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**P141 HOLLOW-FIBER FLOW FIELD-FLOW FRACTIONATION WITH MULTI-ANGLE LASER SCATTERING FOR AGGREGATIONS STUDIES IN COMPLEX PROTEINS**

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**P142 ASSESSING THE POTENTIAL RISKS OF SILVER NANOPARTICLES IN ANTIMICROBIAL APPLICATIONS, USING MINIATURIZED FLOW FIELD-FLOW FRACTIONATION AND MULTI-ANGLE LIGHT SCATTERING**

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**P143 TOWARDS “TRUE” ARTIFICIAL ANTIBODIES BY MOLECULAR IMPRINTING**

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**P144 A HIERARCHICAL APPROACH AS NEW STRATEGY FOR MOLECULAR IMPRINTING OF BIOMACROMOLECULES**

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**P145 NON-INVASIVE STRESS ASSESSMENT IN DOGS BY MEASURING CORTISOL IN SALIVA**

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**P146 NANOPOROUS FUNCTIONALIZED GOLD FOR BIOSENSING APPLICATIONS**

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**P147 BIOMOLECULAR CORONA MAKES ANIONIC NANOPARTICLES LESS ATTRACTIVE FOR IMMUNE CELLS**

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**P148 PROTEOMIC STUDY OF HUMAN COLON ADENOCARCINOMA CELLS EXPOSED TO SIMULATED MICROGRAVITY**

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**P149 DIFFERENTIAL ANALYSIS OF THE PROTEIN CORONA COMPOSITION ONTO LIPOSOMES IN STATIC AND DYNAMIC CONDITIONS**

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**P150 ELECTROCHEMICAL IMMUNOSYSTEM FOR HEPATITIS A VIRUS DETERMINATION**

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**P151 QUANTITATIVE ANALYSIS OF EPERISONE HYDROCHLORIDE AND PARACETAMOL IN MOUSE PLASMA BY USING HPLC-PDA**

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**P152 NANOFORMULATIONS OF BERGAMOT ESSENTIAL OIL FOR *IN VITRO* ANTI NEUROBLASTOMA TREATMENT**

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**P153 MEPS-UPLC-PDA ANALYSIS OF NSAIDs DRUGS IN DIALYZED SAMPLES. OPTIMISATION BY RESPONSE SURFACE METHODOLOGY**

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**P154 OCTREOTIDE AN ANALOG OF SOMATOSTATIN AND GABEXATE MESYLATE IN HUMAN PANCREATIC JUICE SAMPLES MEASURED BY HPLC-DAD-FL DETECTION**

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**P155 IDENTIFICATION BY NANO-LC AND TANDEM MASS SPECTROMETRY OF PROTEINS TRAPPED IN SORBENT CARTRIDGES USED FOR COUPLED PLASMA FILTRATION-ADSORPTION TREATMENTS**

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**P156 DIRECTING SUPRAMOLECULAR ASSEMBLY AT INTERFACES: FROM FUNCTIONAL NANOMATERIALS TO IMAGING PROBES FOR BIOLOGICAL SYSTEMS**

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**P157 DIFFERENCES IN SALIVARY ALPHA-AMYLASE AND CORTISOL RESPONSIVENESS OF PSORIATIC PATIENTS UNDERGOING THE TRIER SOCIAL STRESS TEST**

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**P158 INFLUENCE OF THE SAMPLING PROCEDURE ON THE MEASURED CONCENTRATION OF URIC ACID IN ORAL FLUID**

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**P159 USING MS<sup>E</sup> AS A NEW TOOL FOR QUANTIFICATION IN A GLP REGULATED ASSAY VALIDATION FACILITY.**

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**P160 THE MONITORING OF OCCUPATIONAL EXPOSURE TO ACTIVE PHARMACEUTICAL INGREDIENTS: DETERMINATION OF CHEMICAL TRACERS ON MEMBRANE FILTERS BY NIR/PLS METHOD**

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**P161 TOTAL CONCENTRATION AND BIOACCESSIBILITY OF POTENTIALLY TOXIC ELEMENTS IN AYURVEDIC FORMULATIONS**

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# Plenary Lectures

**IONIC LIQUIDS IN SEPARATIONS AND MASS SPECTROMETRY**

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Room-temperature ionic liquids (RTILs), are a class of nonmolecular ionic solvents with low melting points. Most common RTILs are composed of unsymmetrically substituted nitrogen-containing cations (e.g., imidazolium, pyrrolidinium, pyridinium) or phosphonium cations with inorganic anions (e.g.,  $\text{Cl}^-$ ,  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ). Most of these more common ILs are of limited use analytically. Consequently many ILs containing a variety of cations and anions of different sizes have been synthesized to provide specific characteristics. In this presentation an overview of the structure and properties of ILs and a description of their expanding use in various applications in separations, chromatography and mass spectrometry will be given. A number of studies have appeared indicating that ILs have exceptional promise as stationary phases. They have a dual nature selectivity in that they separate nonpolar molecules as would a nonpolar stationary phase and they separate polar molecules as would a polar stationary phase. Many ILs have exceptional thermal stability. They are being used increasingly in a variety of applications including 2-D GC, enantiomeric separations, the measurement of water in samples/solvents/materials and compact field GC units. ILs have proven to be the best liquid MALDI-MS matrix since we introduced them as such a few years ago. The properties of ILs that make them effective will be discussed. Further, the dications developed for high stability ILs have found another novel use in electrospray ionization (ESI) MS as a reagent for ultra sensitive anion analysis. These will be discussed as well.

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## OPENING NEW ANALYTICAL PATHWAYS WITH BIPOLAR ELECTROCHEMISTRY

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Bipolar electrochemistry is a somewhat unconventional way of performing electrochemical experiments, as it allows carrying out redox reactions on conducting objects present in solution in a wireless way, due to their polarization in strong electric fields. The concept has been known for decades<sup>1</sup>, but undergoes currently a true renaissance in various scientific domains, with applications ranging from analytical chemistry to materials science<sup>2-4</sup>. In this lecture we will illustrate that the approach is a very powerful tool especially for analysis, because many objects can be addressed simultaneously, which opens up interesting perspectives for example with respect to massive parallel screening. We will describe some of the most recent advances<sup>4,5</sup>, either concerning the highly controlled surface modification of micro- and nanoobjects that can act as individual analytical tools<sup>6-11</sup>, or with respect to the design of dynamic systems<sup>12,13</sup>, which are able to show different properties, including for example light emission<sup>14,15</sup>, enzymatic recognition<sup>16</sup> and electronic functionalities<sup>17</sup>.

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## **CHALLENGES TO DETECT AND QUANTIFY OF NANOMATERIALS IN CONSUMER PRODUCTS**

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Today, many consumer products - including food - that contain nanomaterials can already be found on the market. These can be food additives and cosmetics' ingredients. Moreover it can be expected that novel foods and food packaging materials incorporating nanomaterials will continue to be developed. As consumers need to be informed, the presence of nanomaterials requires appropriate labelling.

The regulatory requirements already envisaged for food products and cosmetics necessitate the availability of fit-for-the-purpose analytical methods to detect, quantify and characterise nanomaterials. This does not only apply to individual ingredients or additives, but may also be necessary for enforcement/compliance purposes in final products. As it may be difficult to discriminate purposely added nanoparticles from natural nanoscale structures – especially in complex matrices, such as food and cosmetics - the work of analysts is becoming very challenging.

As the results obtained in the laboratories need to be trustable, reproducible and of high quality, laboratories are requested to follow internationally harmonised and recognised standard methods for analysis which need to comply with quality criteria, e.g. accreditation according to ISO 17025.

This presentation will highlight the challenges for analysts and the need for appropriate quality assurance tools.

## **MEDIATED DNA SENSORS BASED ON SUPRAMOLECULAR AND ELECTROPOLYMERIZED CARRIERS**

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DNA based biosensors offer great opportunities for the fast and sensitive detection of various chemical species specifically interacting with the biorecognition elements, e.g., native DNA, oligonucleotides and aptamers. However, their application for the detection of low molecular compounds is often limited by difficulties in quantification of minor changes of their characteristics resulted from target interaction on the transducer interface. The use of redox probes, quite common for the detection of hybridization events, can be insufficiently sensitive to reach nanomolar detection limits required for many analytes like mycotoxins, carcinogenic factors and pharmaceutical preparations. The use of novel structured materials with mediator functions and branchy flexible structure increases sensitivity of electrochemical DNA sensors due to steric control of target interactions and appropriate changes in electrostatic forces in the reaction layer. This makes it possible to enhance the dynamic range of the analyte concentrations determined and decrease limit of detection to the sub-nanomolar values.

In this review, the approaches to the development of novel electrochemical DNA sensors and aptasensors utilizing electropolymerized and nano-sized supramolecular redox mediators are summarized and discussed.

Two types of electrochemical DNA sensors are considered. In the first case, phenazine dyes were covalently attached to macrocyclic carriers providing steric positioning of redox centers in the surfaced layer. The biosensors were assembled by self-aggregation of charged electropolymerized layers and macrocyclic cores. Well reproducible structure and permeability of the surface layers for low molecular charge carriers and analyte molecules were confirmed by AFM and EIS measurements. Introduction of target species interacting with aptamers or native DNA resulted in limitations of electron exchange within the surface layer resulted in synchronous changes of the mediator currents and charge transfer resistance.

In the second type biosensors, electropolymerized polyaniline and polyphenothiazine layers have been employed as mediators and receptor carriers. Native DNA was entrapped in the growing polymer film in the polymerization stage. Intercalation or oxidative damage of DNA affected packing and redox properties of hybrid film recorded by DC voltammetry and EIS. Examples of appropriate biosensors for the detection of thrombin, mycotoxins, reactive oxygen species, anti-DNA antibodies, cytochrome c, anthracycline and phenothiazine drugs are presented.

# **Premio Giovane Ricercatore**

## **OMIC ANALYSIS OF DIFFERENT COMPLEX SAMPLES: A CHALLENGING BUT POWERFUL APPROACH**

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Among "omic" sciences proteomics and peptidomics are the large-scale study of the structure and function of proteins and peptides in complex biological samples. Such an approach has the potential value to provide understanding of the complex nature of organisms. Current proteomic tools allow large-scale, high-throughput analyses for the detection, identification, and functional investigation of proteomes. Advances in protein fractionation and labeling techniques have improved protein identification to include the least abundant proteins. In addition, proteomics has been complemented by the analysis of post-translational modifications and techniques for the quantitative comparison of different proteomes. However, the major limitation of "omic" investigations is provided by the complexity of biological structures and physiological processes, which pave the path of exploration with various difficulties and pitfalls. The quantity of data that is acquired with new techniques places new challenges on data processing and analysis. This keynote provides an overview of my research activity focusing mainly on the major developments in the field of "omic" sciences, telling some success stories as well as challenges that are currently being faced. In particular, it is principally focused on nanomedicine, peptidomics applied to identification of potential bioactive peptides in food, and phosphoproteomics, to develop new and alternative systems able to enrich phosphopeptides. The common thread will be the prominent role of analytical chemistry applied to the study of complex biological matrices. Due to proteome complexity, there is no single standard method for preparing protein samples for analysis by mass spectrometry. The use of specific fractionation schemes and prudent adoption of methods to increase the number of proteins, able to be identified and quantified, will be discussed. Protocols differ depending on sample type, experimental goals, and analytical method used. Many factors are considered when designing sample preparation strategies, including matrix, type, physical properties, abundance, complexity and cellular location of the proteins. Therefore, the quality and reproducibility of sample extraction and preparation significantly impact the final results.

These advances in proteomics will impact not only on academic pursuits but also on pharmaceutical, biotechnological, diagnostic and food research and development.

# Keynotes

**ON THE KINETIC PERFORMANCE OF COLUMNS PACKED WITH NEW 1.9 MM FULLY POROUS PARTICLES OF NARROW PARTICLE SIZE DISTRIBUTION**

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The evolution of packed column technology over the last ten years has been in the direction of shorter, narrower columns packed with finer particles. Progress in manufacturing and packing technologies have resulted in the standard columns of today being characterized by very high efficiency and large peak capacity suitable for ultrafast separations. In parallel, our understanding of physical phenomena that control column efficiency has progressed considerably thanks to accurate experimental determination of all mass transfer processes that has nowadays become possible. The recent introduction to the market of sub-2  $\mu\text{m}$  fully porous particles characterized by very tight particle size distribution (PSD) and excellent kinetic performance has inevitably rekindled the debate on the importance of PSD on column efficiency.

The kinetic and thermodynamic characterization of columns packed with new 1.9  $\mu\text{m}$  fully porous Titan-C18 particles was performed by means of different chromatographic and non-chromatographic techniques. The traditional study of the dependence of column efficiency on flow rate was done on a UHPLC system optimized in terms of extra-column dispersion. Columns with different length (50, 75 and 100 mm), inner diameter (3.0 and 2.1 mm), pore size (80 and 120  $\text{\AA}$ ) were considered. In the first part of the presentation, we discuss a detailed proof-of-concept study on the kinetic performance of columns packed with new 1.9  $\mu\text{m}$  fully porous monodisperse particles by considering columns of different geometries (length and diameter) and packed with particles of two different average pore size. A large amount of data has been collected by using benzene derivatives as probes in binary water/acetonitrile eluents. Based on this relevant amount of experimental data, the conclusion can be drawn that these new separation media, characterized by a very tight PSD, exhibit very high kinetic performance. For the sake of comparison, the behavior of another commercially available C18 column (characterized by larger PSD) has been also evaluated. In the second part of the work, the kinetic phenomena controlling mass transfer have been considered from a more fundamental viewpoint. This investigation has provided critical data toward some possible explanations for the observed performance of the new particles.

## USE AND ABUSE OF SIGNAL PRE-PROCESSING

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Mathematical pre-processing include a wide number of transformations generally aimed at minimising the unwanted variations that may affect analytical signals, with the result of improving data quality and, consequently, the conversion of data to valuable information.

In particular, it is possible to individuate two main objectives: reduction of random noise, and minimisation of systematic unwanted variations.

Several pre-processing techniques accomplish with more than one point. In some cases, the transformation itself may enhance and aid to resolve the features of complex signals.

Examples of common pre-processing corrections are the standard normal variate transform (SNV) – or row autoscaling [1] – and derivatives of different orders, usually applied in combination with smoothing, to overcome the enhancement of random noise, which is usually characterised by high-frequency slope variations [2].

In addition to the desired corrections, application of mathematical transforms may produce undesired secondary effects. In particular, some transforms may introduce artefacts [3]. Other may complicate interpretation of the final results of signal processing – a risk that is often underestimated.

The desired and undesired effects of the most common signal transforms will be reviewed. Moreover, their effects on the interpretation of the outcomes of common chemometric methods (such as principal component analysis – PCA) will be critically described, and some simple strategies to overcome these hurdles will be presented.

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**CARBON BLACK AS SUCCESSFUL CARBONACEOUS NANOMATERIAL MODIFIER FOR SCREEN-PRINTED ELECTRODES**

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Carbon is present in several allotropic forms ranging from graphite to diamond, through the most recently discovered fullerene, nanotubes and graphene. The latter ones hold a leading role in the current electrochemical sensor scenario, thanks to their unique properties. The presence of CNTs or graphene on the surface of the working electrodes can improve the electroanalytical performances by enhancing the electron transfer between the surface of modified electrodes. In recent years, another interesting carbonaceous nanomaterial is becoming utterly interesting, due to its excellent conductive and electrocatalytic properties: Carbon Black (CB). Here, we present our results obtained in the last five years in the successful use of CB as modifier for screen-printed electrodes towards several analytes such as thiocholine, cysteine, NADH, hydrogen peroxide, and phenol compounds [1]. The high sensitivity of this nanomaterial for thiocholine was exploited to develop a chemosensor for Hg(II) [2] and a biosensor for organophosphorus pesticide detection [3]. Moreover, the suitability of CB in electroanalysis was also explored preparing hybrid nanocomposites with gold nanoparticles for As(III) detection [4], thionine for bis-phenol A [5] and Prussian Blue nanoparticles for hydrogen peroxide. In the latter case, we have demonstrated that different modifications of SPE with CB are able to tailor the dimensions of Prussian Blue nanoparticles, and increase the sensitivity of the sensor. Furthermore, a direct comparison with SPE modified with graphene and CNTs, showed the advantages to use CB in terms of electrochemical properties, cost-effectiveness, capability to easily obtain a stable and homogenous dispersion, demonstrating that CB can be widely employed in the development of nanomodified electrochemical sensors.

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**EARLY DIAGNOSIS OF TROPONIN T BY OPTICAL, LABEL FREE, AND REAL TIME NANOSENSING. A HIGH SENSITIVE POINT-OF-CARE TESTING BY COUPLING EMERGING SYNTHETIC RECEPTORS TO LOCALIZED SURFACE PLASMON RESONANCE (LSPR)**

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Optical biosensors based on Surface Plasmon Resonance (SPR) and its Localized (LSPR) evolution are at the forefront of ultra sensitive detection of clinical biomarkers at nanoscale [1,2,3]. Their label free mode, sensitivity, and selectivity play key roles in this success, but also their optimal results in terms of miniaturization, multiplexing, all-in-one integration, and cheapness are crucial. These features make optical biosensors very promising platforms for point of care tests of last generation [4]. Moreover, coupling of SPR/LSPR transduction with biomimetic receptors may open new interesting detection strategies in biosensing. This keynote presents the last achievements in the field, and will present a case study of interest in clinical diagnostics recently funded by a project (SIR MIUR 2015). It aims to develop a nanobiosensor based on innovative MIP-based receptors coupled to LSPR transduction for the 'high sensitive' detection of cardiac troponin T (hsTnT) for a point of care test (POCT) of last generation. Cardiac TnT in blood is the most specific and sensitive biomarker of acute myocardial infarction (AMI) for its positive contribution to early diagnosis [5]. TnT quantification is routinary in triage protocols of cardiac emergency, according to the current international guidelines, but available point of care tests (POCTs), based on immunoreactions, allow still only qualitative or semi-quantitative detection, far from international requirements [6]. Their use in pre-hospital management of patients (ambulances, medical laboratories, peripheral, country hospitals) is thus still a challenge, albeit their positive diagnostic and prognostic impact has been demonstrated (REF) [7]. High sensitive TnT quantification by standard core laboratory testing remains thus the first choice, if obtainable within 1 hr from the onset of symptoms. The recent appearance of molecularly imprinted polymers (MIPs) for TnT detection suggest a step forward in the research on TnT bioreceptors [8]. In this framework, MIP receptors coupled traditional and Localized Surface Plasmon Resonance (SPR, LSPR) nanotechnology, will possibly open a new POC testing in hsTnT detection on small, portable, mini invasive, and sensitive platforms for early diagnosis of AMI.

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**ANALYTICAL CHARACTERIZATION OF POLYURETHANE FOAMS MODIFIED BY SILVER NANOPHASES. A MULTI-TECHNIQUE APPROACH FOR THE SYSTEMATIC ASSESSMENT OF SURFACE CHEMISTRY, MORPHOLOGY, ION AND NANOPARTICLE RELEASE ISSUES**

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Polyurethane foams modified by photo-deposited silver nanoparticles (Ag-PU) represent one of the outcomes of the national project "PON01\_02210 - Silver" we carried out in the last four years. This antimicrobial material is successfully applied as a key-component of several industrial goods such as air-filtering systems, stuffing for seats, etc. [1, 2]. On the other hand, the widespread use of nanomaterials in commercial goods poses some concerns regarding human and environmental health. As a result, a detailed characterization of Ag-treated materials might be unavoidable.

Here we report the most representative results of the analytical characterization of the composite material in terms of morphology, surface chemical composition, ionic release in contact media, bioactivity, as well as whole nanoparticle release.

Scanning Electron Microscopy (SEM) was used to assess the composite morphology and cross-sectional SEM allowed us to trace the inorganic nanophase distribution and morphology changes at different depths of the foam's surface.

X-ray Photoelectron Spectroscopy (XPS) provided quantitative information about silver surface availability, as a function of the metal precursor concentration in the photo-deposition media [3]. Ag surface chemical state was evaluated by means of its main Auger signal.

Inductively coupled plasma atomization mass spectrometry (ICP-MS) allowed investigating Ag<sup>+</sup> release in contact media such as physiological solutions, as well as slightly acidic media, as a function of the silver overall content in Ag-PU composites.

The potential release of entire nanoparticles from Ag-PU materials was studied by developing a suitable experimental setup for their collection after air filtration with the proposed composites. Collected samples were analyzed by Transmission Electron Microscopy (TEM) to validate release experiments, aimed at ruling out

or quantifying the extent of whole particle release by antimicrobial foams under real-life usage conditions.

The different analytical results concur in demonstrating that Ag-PU potential efficacy (in terms of Ag surface content, in-depth distribution and ionic release) as well as the corresponding bioactivity are easily tunable by controlling the sample deposition parameters. Conclusions will be drawn about the safety and efficiency of the mentioned Ag-PU composites.

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**APPLICATIONS OF THE CHEMICAL EQUILIBRIUM MODELLING EXPERTISE**

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Our experience in equilibrium studies has mainly regarded the evaluation of protonation and complexation constants, principally by potentiometry, molecular absorbance spectrophotometry and calorimetry. Nowadays the scientific approach to this topic is changed, involving further instrumental techniques, that can provide complementary information, such as NMR, EPR, ESI MS, fluorescence, separation techniques. The information obtained through these techniques or combination thereof affords the species forming in solution as well as their stability constants. In turn, the skills in the chemical speciation modelling are fundamental for the rigorous interpretation of i) metal ion – ligand complex formation, ii) charge-transfer complexes (CT) between organic molecules, iii) binding of metal ions or organic molecules to macromolecules, iv) bio-inorganic/organic processes, v) heterogenous equilibria. The application of new techniques and the multidisciplinary approach to this investigation lead to widen the application fields of the equilibrium studies.

In this note I shall review some of the fields that still need to be examined by an expert of chemical modeling.

## **ANALYSIS OF NEW PSYCOACTIVE SUBSTANCES IN BIOLOGICAL MATRICES BY PLE FOLLOWED BY LC-MS/MS**

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Drug abuse is a growing global problem that affects people of all ages. Recently new psychoactive substances (NPS) often sold as “legal-highs” appeared in the illicit market.

In our laboratories different analytical methods for the determination of several NPS were developed for different biological matrices (plasma, oral fluids (OF), urine and hair); these methods are focused to the simultaneous identification and quantification of 48 NPS, including cathinones, phenethylamines, synthetic cannabinoids and several metabolites. A part of the research activities was carried out in RIS-Carabinieri laboratories.

For plasma a rapid sample preparation was performed: 250  $\mu$ L the sample was mixed with ACN/MeOH for protein precipitation. The extraction of analytes from hair was based on pressurized liquid extraction (PLE) followed by SPE, in order to obtain both reduction of matrix effect and enrichment of the analytes [1]. For plasma and hair the analysis was carried out by means of UHPLC-HRMS/MS by Orbitrap mass spectrometer.

Urine preparation was carried out on 90 $\mu$ L of sample, incubated with  $\beta$ -glucuronidase and then cleaned up by SPE followed by HPLC-MS/MS. This procedure provides an efficient extraction/sample clean-up.

Oral Fluids has become a valuable biologic specimen for toxicological analysis because of easy and non-invasive collection procedures.

The sample preparation is based on microextraction by packed sorbent (MEPS), a novel technique which is based on the miniaturization of solid phase extraction (SPE) [2]. The effectiveness of the clean-up was proved by low ion suppression in ESI-MS/MS, evaluated by post-infusion analysis, which was below 15% for all the analytes.

The presented methods were fully validated according to the Scientific Working Group for Forensic Toxicology (SWGTOX) guidelines.

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## **ELECTROCATALYTIC COATINGS IN AMPEROMETRIC SENSING: ADVANTAGES AND CRITICISMS**

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The most critical aspect leading to the development of an efficient amperometric sensor lies in the choice of the sensitive element, which constitutes the interface of the device with the analyte. In this respect, it is not excessive to affirm that a notable portion of the progresses in amperometric sensing should be acknowledged to the advent of novel electrode coatings [1,2]. They range from organic to inorganic materials, possessing surface structures that are properly described on meso- or nanoscale. The number of possible electrode coatings is further enriched by the introduction of composite materials, aiming not only at combining the properties of the individual components, but also at taking advantage of the possible synergic action between them.

The talk aims at giving a quick overview of the main electrocatalytic coatings used in electroanalysis. Redox mediators, conducting polymers, metal and carbon nanosized materials, together with the relevant composites, will be considered with particular attention. The exam will be addressed to account for the main advantages afforded by the use of these materials in electroanalysis. On the other side, the main critical points that researchers have to overcome when developing efficient electrode coatings for amperometric sensing will be also considered: the stability of the sensitive element on the electrode surface, the optimization of the deposition parameters in respect to the performance of the resulting sensor system, the correct definition of the characteristics of the coating from electrochemical, spectroscopic and microscopic investigations, the definition of the performance of the sensor in real matrices. These constitute fundamental points of the complex process toward the development of effective amperometric sensor systems.

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## **CHALLENGES IN FOOD PROTEOMICS FOR THE SELECTION OF LOW TOXICITY WHEAT GENOTYPES TOWARDS CELIAC DISEASE PATIENTS**

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Owing to its extensive use in human diet, wheat is among the most common causes of food-related allergies and intolerances. Gluten proteins and particularly the gliadin fractions represent the main factor triggering celiac disease. Given the extremely high structural heterogeneity of gliadins, generated by amino acid insertions, deletions and substitutions, the physico-chemical properties of gliadins can vary significantly among wheat genotypes (species, cultivars and breeding lines) influencing in parallel the immunoreactive properties and the susceptibility to enzymatic treatment [1]. Therefore, the structural characterization and the correlation with relevant toxicity, by tracking the fate upon gastrointestinal digestion of wheat-based commodities [2], gains significance to deepen the knowledge at the molecular level of the immunological pathway and to identify naturally low toxic wheat species and/or efficient detoxification technologies.

Recent development in proteomics have contributed to give insights in this field, although the analytical capabilities of the proteomic approach are challenged by the complexity of the wheat seed proteome and particularly of the gluten protein fraction. Limited database entries available, complexity arising from sets of homologue proteins, large occurrence of repeated motifs, very low number of basic residues for tryptic hydrolysis represent drawbacks that complicate the comprehensive proteomic cataloguing of the gluten proteins. These challenging issues can only be addressed by the use of integrated, up-to-date analytical approaches, which together constitute the platform of modern food proteomics, and where a pivotal role is played by mass spectrometry.

The authors acknowledge the project SIR 2014 “S. Wheat Pro. - Proteomic characterization of Selected durum Wheat cultivars for PROduction of low toxicity-food products towards celiac disease patients (RBSI14QQ1W)”

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**NATURE-INSPIRED DNA-BASED SENSORS**

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Here I summarize the most recent results achieved in the laboratory of biosensors and nanomachines towards the development of DNA-based switches and sensors for the detection of clinically relevant protein targets. The inspiration behind our approach is derived from nature's sensing systems, which employ nanometer-scale protein and nucleic-acid-based "switches" to detect thousands of distinct molecules (including disease markers) in real time within complex physiological environments. By mimicking this sensing strategy we have developed during recent years several optical and electrochemical DNA-based sensors for the detection of specific DNA sequences, antibodies, proteins and aptamer's targets. Critically, because the signal of these sensors is induced only by the formation of a highly specific probe-target complex which triggers a specific conformational change, our sensors work well even when deployed in complex samples. Given these attributes, the optical and electrochemical DNA-based sensors we have developed may prove of significant utility in a range of applications, including drug screening, cancer diagnostics, and developmental biology.

## CHELATION THERAPY IN METAL INTOXICATION

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Chelation therapy is a consolidated medical procedure used primarily to reduce the toxic effects of metal ions on human tissues. Its application spans a broad spectrum of disorders, ranging from acute metal intoxication to genetic metal-overload diseases [1-3]. The use of chelating agents can be compromised by a number of serious side effects, mainly attributable to perturbed equilibrium of essential metal ion homeostasis and dislocation of complexed metal ions to dangerous body sites. For this reason, chelation therapy has been limited to specific critical and otherwise untreatable conditions and needs to be monitored within an appropriate clinical context. The essential properties of a chelating agent, based on both chemical and biomedical considerations, have been better and better defined through the years. Some requisites are schematically sketched in the following: high stability of the formed complexes; selectivity toward the target metal ion; no disturbance of the homeostasis of essential metal ions; high exchange rate of metal between endogenous ligands and chelating agents; favorable pharmacokinetics; slow biochemical metabolism; favorable toxicity profile of chelating agent and its complexes. Some of the above traced requirements will be discussed in some detail, pointing out the interconnections between them.

A second purpose of this communication is to describe how a “false chelation therapy” has historically developed. In fact, despite the limited approved indications, advertisements for the treatment of numerous other conditions can easily be found on the web. Although these treatments have no scientific basis, they are proposed to the public in such an appealing way that it may be difficult to effectively counteract the phenomenon.

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# **Oral Communications**

## APPLICATION OF 3-WAY PRINCIPAL COMPONENT ANALYSIS FOR EVALUATING YOGURT STABILITY

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Color, texture and aroma are key elements of a consumer's buying decisions, thus, monitoring the stability of these features throughout the entire period of yogurt validity is fundamental for dairy product producers. Color, aroma and texture deteriorations are due to changes in the physical, chemical and microbiological composition of yogurt but especially microbiological analysis of yogurt is expensive and time consuming.

In this study, UV-VIS spectroscopy was applied as a rapid and alternative technique to traditional analytical methods, to monitor the stability of yogurt up to 49 days of storage at 4 °C.

UV-VIS spectroscopy was employed with an integrating sphere for specular and diffuse reflectance measurements and, for each yogurt, color stability during storage time was evaluated in terms of CIELAB color space values [1].

In order to evaluate the texture and aroma changes, rheological curves and pH values of yogurt during storage were determined once a week for the entire period.

The information contained in the 3-way UV-VIS and rheological data sets was extracted using multivariate data analysis and specifically Tucker 3 [2-4] as a multi-way decomposition method.

It was interesting to note that the time-related information contained in the UV-VIS and rheological data was not visible by simply comparing the profiles of signals, partially visible in the 2 way Principal Component space, and very clear in the Tucker 3 models.

Color, texture and aroma of yogurt samples were also evaluated by a consumer acceptance test. The scores of the assessors were in good agreement with the results of 3-way PCA performed on the rheological measurements and the UV-VIS spectra.

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**SIMULTANEOUS ANALYSIS OF INTACT GLUCOSINOLATES AND CORRESPONDING ISOTHIOCYANATES BY LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY IN STARTING BIOMASSES AND ENRICHED BAKERY PRODUCTS.**

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Glucosinolates (GLS) are nitrogen and sulfur-containing secondary metabolites found mainly in the order of the *Brassicaceae*. Glucosinolates are hydrolyzed by endogenous thioglucosidases (myrosinases) to produce isothiocyanates (ITC), which showed high anticancer activity. Due to their beneficial effects, different functional foods containing GLS were developed. In this context, it is very important to control GLS amount and stability into the functional food to be produced.

The only existing ISO procedure [1] for GLS analysis consists in their conversion into desulphoglucosinolates followed by quantification by HPLC-UV. Therefore, a faster and more robust method for the direct analysis of intact GLS would be very useful to monitor GLS content of a functional food during all stages of its production.

A new HPLC-ESI-MS/MS [2] method for the simultaneous determination of the glucosinolates Glucoraphanin and Glucoerucin and the corresponding isothiocyanates Sulforaphane and Erucin was developed and applied to quantify these compounds in *Eruca sativa* seeds and functional foods. The method was validated following the ICH guidelines [3]. Replicate experiments demonstrated good accuracy (bias < 10%) and precision (CV% < 10%). Detection and quantification limits were in the range of 1 – 400 ng/mL. Calibration curves were validated on concentration ranges from 0.05 to 50 µg/ml. The validated method was applied to the simultaneous determination of glucosinolates and isothiocyanates in bakery products enriched with glucosinolates and to evaluate glucosinolates amount and stability after different industrial processes, from the choice of the biomasses to the final product.

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**COMPARISON BETWEEN BERBERINE AND BERBERRUBINE BIODISTRIBUTION AFTER ORAL ADMINISTRATION IN RATS BY HPLC-ES-MS/MS**

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Berberine (BBR) is an isoquinoline alkaloid isolated from several herbal medicines that exhibits a multi-target activity [1]. Despite its pharmacological effect, the bioavailability of BBR was very low. As well as BBR, also its primary metabolites, particularly Berberrubine (M1) showed a cholesterol-lowering effect. The plasma concentration of M1 was ten times higher than BBR and others metabolites [1]. Recently, several studies have been carried out to explain how BBR, so poorly bioavailable, still exhibits relevant pharmacological activities. Previously we demonstrated that M1 could tautomerized in its more lipophilic quinoid form, which accumulate in systemic compartment more than BBR [1]. In order to demonstrate the *in vivo* tautomeric equilibrium of M1, experiments on rat model with external biliary fistula were carried out. Specifically, M1 has been administered at a single dose of 10mg/kg and compared to BBR administration. BBR, M1 and their potential metabolites have been analyzed in plasma, liver and bile by a validated HPLC-ES-MS/MS after sample clean-up. Preliminary data show that M1 is more efficiently secreted in bile than BBR ( $SB_{max}$  of 19.6 and 3.3 nmol/min/kg respectively) and poorly metabolized by the liver. The plasma levels of M1 are higher when it was directly infused ( $C_{max}=11.8 \mu M$ ) and when it was recovered as hepatic metabolite after BBR administration ( $C_{max}=0.085 \mu M$ , time 120 min). These data suggest that M1 could be highly conserved in enterohepatic circulation thought to be actively absorbed in the ileum in its neutral and more lipophilic quinoid form by the keto-enol tautomerism occurring in the intestine at a  $pH>6$ . Then the quinoid form of M1 could be reabsorbed by passive non ionic transport along the entire intestinal tract resulting in a higher concentration in blood. The use of M1 as a drug could be a benefit avoiding the metabolic hepatic pathway producing a more constant and efficient systemic exposure compared to BBR administration. Studies on the relationship with biomarkers of different diseases are currently underway for M1 in enol and quinoid form to better explain its potential benefic as a drug.

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## **COUPLING OF HIGH TEMPERATURE LIQUID CHROMATOGRAPHY TO ICPMS FOR THE DETERMINATION OF ARSENIC AND SELENIUM SPECIES RELEVANT FOR FOOD SAFETY ASSESSMENT**

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Although HPLC/ICPMS is the analytical technique of choice for elemental speciation analysis, this coupling still suffers from the low tolerance of the detection system to mobile phases with high salt content or organic solvents, thereby motivating the search for alternatives.

High temperature liquid chromatography (HTLC) is an high-performance separation method where the column is heated in an oven to take advantage of the effect of high temperatures on the chromatographic separation, such as the shortening in the retention times, the reduction in the mobile phase polarity and viscosity, the possibility to avoid organic solvents and to work with 100% water as the mobile phase.

Consequently, the HTLC/ICPMS hyphenation could optimally combine the advantages of HTLC as a separation technique with the advantages of ICPMS as a powerful detector.

The aim of the present work, carried out in the context of the Project PRIN-2010AXENJ8, was to explore the potential of HTLC/ICPMS for the determination of arsenic and selenium species.

As regards selenium, a new method has been developed for the quantification of selenosugars and trimethylselenonium ion in urine samples. These compounds are very important because they are the major selenium metabolites in human urine and their quantification can provide useful information on the transformations that take place in the body producing beneficial or detrimental effects. The method has been optimized, compared to conventional HPLC/ICPMS and finally applied to the analysis of urine samples from two volunteers before and after ingestion of Brazil nuts or selenium supplements.

The case of arsenic is also very interesting because its speciation is essential to assess its actual toxicity. Therefore, a new HTLC/ICPMS method has been developed to quantify arsenic compounds with different toxicity, such as arsenite, arsenate, dimethylarsinic acid, monomethylarsonic acid, arsenosugars and arsenobetaine. The developed method has been applied to the analysis of representative samples of interest in the food safety assessment field, including seafood and rice products.



## **SYNTHESIS AND CHARACTERISATION OF MODEL Ag/polymer SYSTEMS FOR THE ASSESSMENT OF SILVER RELEASE FROM ANTIBACTERIAL PACKAGING**

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Due to their well-known antibacterial properties, silver nanoparticles (Ag NPs) find applications in various fields, ranging from surgical tools to food packaging. Although there is a wide literature regarding Ag NPs toxicity on bacteria and also on their potential hazards for human health, the intimate antibacterial mechanism of action of Ag NPs is still widely studied. In the case of food packaging it is fundamental to assess the release of Ag NPs and/or Ag ions to food because the former ones are potentially dangerous for human health.

To overcome the variability induced by the different packing preparations (the utilization of “breathable” and releasing resins, as an example) we decided to study a way to have Ag NPs implantation on a polymer film without the utilization of any other resin. The apparatus we finally developed for this purpose implies a plasma source for the formation of Ag NPs (10-15 nm) which are accelerated in a gun trough a triggered high pressure pulsed valve. In this way a supersonic beam of Ag NPs is generated: the kinetic energy of such Ag NPs is sufficient to implant them on a polymeric target. The principles of this preparation method are described in the literature [1,2]. The Ag NPs/polymer specimens were prepared with a gradient Ag concentration to study the differential release of silver in a single specimen.

Here we would like to present the features of these model materials as determined by electron microscopy (ESEM, HRTEM) and by laser ablation ICP-MS. Preliminary data on leaching tests will be also presented: data refers to ICP-MS determination of bulk Ag concentration in leaching solutions together with laser ablation concentrations profiles recorded on Ag NPs/polymers.

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**USE OF A LC-DAD-QTOF SYSTEM FOR THE IDENTIFICATION OF MARKER COMPOUNDS IN ARGENTINEAN *ZUCCAGNIA PUNCTATA* AND RELATED PROPOLIS**

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The characterization of the chemical profile of bioactive phenolic compounds in *Zuccagnia punctata* was accomplished by LC coupled to both DAD and QTOF detection system.

The use of C18 and pentafluorophenyl (PFP) columns with various chromatographic conditions was optimized in terms of efficiency and selectivity. The use of a PFP column with water and methanol acidified with 1 mM formic acid in ESI negative acquisition showed the highest performance mainly towards caffeic acid derivatives and isobaric positional isomers of flavonoids. The developed method ensured a straightforward approach for target, suspect and non target analysis of the phenolic fractions of bioactive plants, overcoming time-consuming semi-preparative procedures. *Z. punctata* and four propolis samples collected where *Z. punctata* grows were analyzed. Fourteen compounds never mentioned before for this shrub were identified for the first time, among them 4'-hydroxy-2'-methoxydihydrochalcone, 2',4'-dihydroxydihydrochalcone and 1-methyl-3-(4'-hydroxy)phenyl propyl p-coumaric acid ester resulted as major components. Only the two propolis collected in Del Monte phytogeographical region showed large amounts of the major bioactive molecules present in *Z. punctata*. In the absence of pure standards, this approach allowed to perform a rapid screening of plant and propolis, ensuring the possibility to selectively compare their chemical profiles. Some biomarkers of *Z. punctata* was proposed for the standardization of *Z. punctata*-type propolis.

## **PEDOT MODIFIED ELECTRODES FOR THE DETERMINATION OF COLOUR INDEX AND POLYPHENOL CONTENT IN WINES**

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Polyphenols are naturally occurring compounds found largely in the fruits, vegetables, cereals and beverages, among which wines. In this last case, many of the sensory attributes, such as colour and mouthfeel, are affected by the polyphenolic content; furthermore, the determination of this group of compounds can help to identify variants on type and differences in winemaking and maturation processes. The characterization of a wine by its total phenolic content (TPP) and by its colour index (CI), which is determined by the presence of a specific class of polyphenols, i.e., anthocyanin, is hence of great importance. The setup of new devices and methods for rapid, cheap and reliable analysis of TPP content represents an emerging topic, to which electrochemistry can give important contributions.

In this presentation, we show the first results collected by using polyethylenedioxythiophene (PEDOT) modified electrodes for the estimation of TPP content and of CI in different samples of wines. Among the several advantages offered by PEDOT-coated electrodes, the possibility to work properly in aqueous media make them attractive for direct analyses of food matrices, as already demonstrated in our previous studies and in Refs. [1,2]. In the preliminary part of this study, differential pulse voltammetry (DPV) and spectrophotometric measurements have been performed in model wine solutions containing different amounts of red grape skin extract powder (oenocyanin - EC). PEDOT-modified electrodes used in properly diluted wine solutions, buffered at different pH values, give rise to repeatable DPV signals in which a well-defined current peak related to the EC content is detectable. A good correlation is found of the current intensity with the TPP content, as well as with the CI measured by spectrophotometric methods.

In the second part of the study, the correlation curves previously cited have been used for the determination of TPP content and of CI in commercial wines. The comparison between TPP and CI values obtained by the electrochemical and by the spectrophotometric methods is definitely satisfactory, giving sound reasons to go forward in this study.

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**QuEChERS METHOD IN THE DETERMINATION OF POLY(HYDROXYALKANOATES) IN BACTERIA BY ANALYTICAL PYROLYSIS: TOWARD AN ON-LINE MONITORING OF BIOTECHNOLOGICAL PROCESSES**

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Poly(hydroxyalkanoates) (PHAs) are polyesters produced by several bacterial strains and formed by saturated short chain hydroxyacids. From a practical point of view, the need to obtain effective, stable and high quality PHAs production usually requires long microbial acclimatization times. Consequentially, a huge number of systematic determinations of PHAs content and microbial community characterization are needed; therefore it is important to identify fast and reliable analytical procedures able to provide both of these parameters for a real time monitoring of the production process.

The aim of this work is the development of a fast method for the quantitative determination of PHAs and their monomeric composition by using pyrolysis coupled with GC-MS analysis. In fact, under pyrolysis, PHAs are degraded in high yield (>40%, w/wPHA) into the corresponding 2-alkenoic acids (e.g. crotonic acid from polyhydroxybutyrate) [1]; moreover, under these conditions, other bacterial-strain specific markers (e.g. long chain fatty acids) can be detected [2]. In the developed protocol, the sample was directly subjected to low temperature thermal treatment (300°C for 30 min) in a closed vial and reaction products were analyzed by GC-MS. The method was firstly optimized on pure polymers and then applied to bacterial samples deriving from both mixed microbial cultures or selected strains, containing various types and amounts of PHAs.

The QuEChERS method provided RSD <15% range, limit of detection of 100 µg (1% PHAs in biomass), and results comparable to that of conventional methods ( $R^2 = 0.9855$ ), but with minimal sample pretreatment.

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**ANALYSIS OF ANTITHYROID DRUGS IN SURFACE WATER BY USING LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY**

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Antithyroid drugs (ATDs) are heterocyclic compounds containing a thionamide functionality able to produce a decrease in the production of thyroid hormones T3 and T4. For this reason, ATDs have been in use for more than half a century in human medicine for the management of hyperthyroidism as well as in veterinary medicine to treat companion and farm hyperthyroid animals. Moreover, in the last decade there has been a strong suspicion about their illicit administration to obtain a quick fattening with commercial purpose.

ATDs are associated with a variety of minor side effects and potentially life-threatening. The FDA has categorized these drugs as class D agents because of the potential for foetal hypothyroidism. For these reasons, there is a world-wide agreement on the ban of these drugs in animal husbandry.

Humans and animals excrete un-metabolized ATDs in urine or faeces; thence, these drugs can reach sewage treatment plants and enter surface waters if they escape degradation. Although the number of human prescriptions is steadily increasing, currently, there are not analytical methods to verify the potential contamination of the different environmental compartments. Certainly, the unique physico-chemical properties of ATDs (high polarity, amphoteric nature, small molecular weight and tautomeric forms) make this a demanding task to be undertaken.

This work describes development and validation of a new method for the simultaneous determination of six antithyroid drugs in surface waters using liquid chromatography–triple quadrupole mass spectrometry (LC–MS/MS). Sensitivity and selectivity of the multiple reaction monitoring (MRM) analysis allowed applying a simple preconcentration procedure and “shooting” the sample into the LC-MS/MS system without any other treatment with recoveries higher than 75%. The adequate values obtained for all the validation parameters studied allowed its successful application to the analysis of ATDs in surface water samples collected from the Tiber river basin and three lakes of Lazio (central Italy), selected on the basis on the different anthropic impact. The most frequently detected compound was tapazole, one of the most common ATDs used in human medicine but also thiouracil and mercaptobenzimidazole were detected in some of the analysed samples.

## **ALTERNATIVE RENEWABLE BIOFUEL: CHARACTERIZATION OF VINE SHOOTS**

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The issues of global warming and depletion of fossil fuels have reemphasized the importance of energy recovery from wastes [1]. Biomass is the organic matter derived from trees, agricultural crops and other living plant material. The use of biomass for energy does not increase carbon dioxide emissions and does not contribute to the risk of global climate change. In addition, using biomass to produce bioenergy is often a way to dispose of waste materials that otherwise would create environmental risks.

Vine shoot is the major sub-product of vineyards, as it is produced from the annual pruning, with production of approximately 2–4 tons/ha in Piedmont. They are generally shredded and then buried, or burned directly on the sideline, constituting an additional charge for the farmer. This solution is the fastest one but not the best one, economically and environmentally. Thus, one of the biggest challenges for wine-producing regions is to create alternatives for processing the vast amount of grape waste generated during harvest season [2].

The present study has characterized vine shoots to reevaluate them as biofuel. Two samples of vine shoots from Asti (moscato) and Sardinia (cannonau, cagnulari e vermentino) were analyzed. Proximate analysis (ash content, volatile matter, fixed carbon), elemental composition (Al, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Zn, S, P e Si) and higher heating value (HHV) were determined.

Proximate analysis results were similar for both vine shoots. The ash content and the HHV were approximately 3% and 4518 kcal/kg for both of them. These two parameters make biomass suitable for using it as a biofuel despite its medium quality. S, Cl and heavy metal contents were low. In particular, the element contents were higher for Asti vine shoots than Sardinia ones except for the Na, Cl, Cr and As contents.

One of the best ways of using this waste is to convert it into fuel for generating heat and electricity on a small scale, to supply the needs of vinegrowers themselves or nearby locations.

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## ICP-MS-BASED ISOTOPIC ANALYSIS OF ENVIRONMENTAL SAMPLES COLLECTED FROM POLAR REGIONS

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Isotope ratio data of appropriate analytical quality are able to provide valuable information in different fields of research, including archaeometry, geochemistry, forensics and environmental sciences.

In particular, the measurement of lead isotope ratios in environmental samples is very useful for assessing its origin and long-range transport pathways and to distinguish the relative contributions of natural and anthropogenic sources. The accurate measurement of these isotope ratios can, however, be quite challenging when the analytical concentration is low and the sample size limited, as frequently occurs in polar environmental studies.

Recently, we have developed different analytical protocols, enabling us to measure lead isotope ratios in a number of environmental sample types, including atmospheric particulates, surface snow, marine suspended particulate matter and sediment. Single- and multi-collector inductively coupled plasma-mass spectrometry (ICP-MS) were employed in this context, in combination with conventional and high-efficiency sample introduction systems. The analytical methods were optimized using multivariate approaches, and the procedures developed were characterized in terms of analytical working range, interferences and uncertainty accompanying the measurement data. Finally, the methods were applied in the context of polar studies addressing both the Arctic (Ny-Ålesund, Svalbard Islands) and Antarctica (Terra Nova Bay and Dome Concordia) [1-3].

The main features of the analytical procedures developed and representative results for the marine environment and the atmosphere will be presented and discussed.

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**PASSIVE SAMPLING AND STIR BAR SORPTIVE EXTRACTION: TWO INNOVATIVE APPROACHES FOR THE DETERMINATION OF NONSTEROIDAL ANTI-INFLAMMATORY DRUGS AND OTHER POLAR CONTAMINANTS IN WATER**

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The protection of the aquatic environment requires a constant monitoring activity and new, more effective sampling/preconcentration techniques are necessary. In fact, besides well known pollutants as pesticides, new compounds used in everyday life, the “emerging pollutants”, need to be determined. For example pharmaceuticals are not entirely absorbed by human body, reaching the aquatic compartment through the effluents from wastewater treatment plants. The very low concentration level and possible matrix interferences represent the main analytical problems; so, highly sensitive and selective detection techniques must be preceded by reliable sampling and preconcentration steps.

Two different innovative approaches have been developed in our laboratory for the determination of polar contaminants in water such as nonsteroidal anti-inflammatory drugs (NSAIDs): stir bar sorptive extraction (SBSE) and passive sampling, followed by liquid chromatography-tandem mass spectrometry.

SBSE was developed by comparing classical PDMS stir bars with new polar phases (Polyacrylate and EG-Silicone); main SBSE parameters optimized to attain high enrichment, then analytes were back-extracted using liquid desorption under ultra sonication. The SBSE-LC-MS/MS method provided satisfactory figures of merit (NSAIDs showed LODs in the range 7.5 - 71 ng L<sup>-1</sup>) and was successfully applied to real samples collected from river water and wastewater effluents.

The passive sampling approach was carried out by using Polar Organic Chemical Integrative Sampler (POCIS); samplers were deployed for two weeks in river and tap water, allowing the detection of analytes at the ultra-trace level. Using the sampling rates values obtained by means of a simple calibration system developed in our lab, Time Weighted Average concentration of NSAIDs in river water was estimated in the range 0.33-0.46 ng L<sup>-1</sup>.

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## **HINTS ON PAST SEA ICE CHANGES AND SOLAR ACTIVITY FROM TALOS DOME SITE (EAST ANTARCTICA)**

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The site of Talos Dome (TD - East Antarctica, 159° E 72° S, 2316 m a.s.l.), revealed to yield relevant information on past environmental and climatic variability on different timescales due to favourable features such: high accumulation rate (allowing the chemical species preservation) and geographical location (sensitive to atmospheric transport processes occurring on the regional to global scale). Here we show two chemical records from TD site, sea salt Na<sup>+</sup> (ssNa<sup>+</sup>) and nitrate, focusing on their potentiality of providing information on past sea ice and solar activity.

Although sea ice is a key component of the polar climate, a direct knowledge of its variability is limited to the satellite monitoring era and, for earlier times, one has to rely on proxy data. ssNa<sup>+</sup> record from ice cores has been long proposed as such a proxy but, in order to reliably use it, a validation with the available direct data for current times is mandatory. At this purpose, ssNa<sup>+</sup> record from TD firn cores was compared with satellite data of Sea Ice Extent (SIE) in the whole Antarctic Ocean and in different sectors in the 1978-2003 time period. A good agreement was observed especially considering the Ross Sea and Indian Ocean sector, which appears to control ssNa<sup>+</sup> concentration in the marine aerosol reaching TD during selected periods.

As concerning solar activity, a better knowledge of its long-term variability is crucial for solar physics, as well for environmental and climate sciences. Continuous direct records are limited to the past four centuries, so that for longer timescales one has to rely on indirect proxies, such as cosmogenic nuclides <sup>14</sup>C and <sup>10</sup>Be, stored in natural archives. Nonetheless, a difficulty in such a reconstruction by using cosmogenic isotopes is due to the complex signal they provide (containing information on production rate and also on geochemical system effects) and to significant discrepancies on millennial time scales, hindering the knowledge of solar activity at this time scale. At this regard, a significant positive correlation between nitrate content in TD (TALDICE) ice core and the flux of galactic cosmic rays, as reconstructed from radiocarbon INTCAL <sup>14</sup>C and GRIP <sup>10</sup>Be records, was found along the Holocene on multi-centennial and millennial timescales. Moreover, Schwabe (11 yr) and Gleissberg (55-100 yr) solar cycles were shown to be present in the last two centuries of nitrate dataset. These evidences support TALDICE nitrate record as a potential new proxy of past solar activity.

**SOURCES, TRANSPORT PROCESSES AND CLIMATIC IMPACT OF POLAR AEROSOL. A MULTI-YEAR ITALIAN EXPERIENCE.**

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The aerosol plays a key role in the local to global distribution of natural and anthropogenic chemical components emitted into the atmosphere from marine and terrestrial environmental sectors. In particular, the size distribution and chemical composition of aerosol particles affects the climate through complex feedback processes between climate forcings and environmental responses, by the interaction with the solar irradiation (scattering and absorption processes) and as CCN sources. Besides, anthropogenic pollutants can be quickly transported from the source areas to the deposition sites that could have a very higher vulnerability for the atmospheric contaminants. Due to the large uncertainties on the knowledge of the quantitative and qualitative effects of the aerosols in the Polar Regions and the high vulnerability of the polar ecosystems, with particular attention to the effect of the present climate change in the Arctic, several measurements and sampling campaigns were carried out both in Antarctica and in the Arctic since 2005 by the Italian aerosol community.

In order to understand the main atmospheric processes possibly leading anthropic and natural aerosol components in inner Antarctica, a continuous all-year-round sampling of size-segregated aerosol were carried from 2005 to 2013 at Dome C (East Antarctica; 75° 60' S, 123° 200' E, 3220 m a.s.l. and 1100 km away from the nearest coast). In the Arctic, a continuous all-year-round sampling campaign is ongoing since 2010 at Thule (North Greenland). Contemporaneously, "summer" (March to September) aerosol was annually collected at Ny Alesund (Svalbard Islands, Norway; 78°56' N, 11°56'E; 50 m a.s.l.), together with size-distribution measurements in the nano- and micro-metric ranges. Besides, shorter measurement and sampling campaigns were carried out by using a tethered balloon, up to about 1.000 m altitude, in order to study the effect of the PBL dynamics on the aerosol atmospheric load and chemical composition.

Chemical analysis includes: Ion Chromatography (inorganic anions and cations, selected organic anions); elemental analysis (PIXE, ICP-AES and ICP-MS for selected metals, including REEs); Pb isotopic composition; thermo-optical analysis (Elemental/Organic Carbon fractions - EC/OC).

Besides, continuous measurements of particle size-distribution (TSI-SMPS and TSI-APS; 6 nm – 20 µm; 10 min resolution) and Black Carbon (by Particle Soot Absorption Photometry – PSAP) were carried out during the sampling periods.

Here, we report the most relevant results obtained from the sampling campaigns carried out in Antarctica and in the Arctic.

## **PYROLYSIS AND GASIFICATION OF WOODSTOCKS: ANALYSIS OF ORGANIC COMPOUNDS**

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Lignocellulosic biomass is currently attracting much attention as a renewable energy source. Thermochemical processes commonly used to produce energy from biomass are pyrolysis and gasification [1]. Solid (biochar), liquid (biooil and tar) and gaseous products derived from these processes may contain hazardous organic compounds, such as phenols and PAHs, depending on experimental conditions [2].

Since biochar can be used as a soil amendment to improve soil functions and may concurrently act as carbon sequestrator, and biooil is regarded as an alternative to fossil fuels, they can release organic compounds in the environment.

The aim of this work is to assess the formation of organic compounds in relation to the main process parameters: temperature, residence time, presence of oxygen [2].

The analysis of biooil and tar, and biochar extracts was made by GC-MS, while qualitative identification of main sorbed volatile organic compounds (VOCs) on biochar was conducted by purge and trap desorption coupled to GC-MS [2].

Some samples were obtained in laboratory from the same feedstock (woody biomass) at different temperature, in a range between 400 and 900°C, both in anaerobic and aerobic conditions. Others derived from commercial or industrial plants; in these cases exact production parameters were not always known.

Preliminary results showed that commercial/industrial biochar samples have more VOCs than ones obtained in laboratory, e.g. methylnaphthalene was not found in the laboratory char samples [3]. Biooil samples produced in laboratory at different temperatures have similar qualitative composition. However, some organic compounds, which were found in all biooil samples, were in different percentage depending on temperature, such as alkylphenols and alkoxy phenols.

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## **SYSTEMIC INSECTICIDES FROM CORN COATED SEEDS. A LC-HRMS STUDY ON METHIOCARB AND ITS METABOLITES IN GUTTATION DROPS**

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The seed coating with systemic pesticides is a worldwide used agronomic practice. Recently, in EU some neonicotinoids (and fipronil) have been banned as seed coating insecticides in crops that are attractive for honey bees [1]. As a consequence, the methylcarbamate methiocarb has been authorized and largely used as an alternative pesticide for the corn seeds coating.

It is well established that guttation drops of plants obtained from treated seeds might contain high concentration of systemic pesticides [2]. In the case of corn seeds coated with neonicotinoids, highly contaminated guttations (10-1000 mg/L of insecticide) are released in the first weeks after the seedling emergence [3]. These levels can cause acute toxicity in insects, included pollinators like honey bees. Therefore, guttation drops must be carefully considered in the assessment of the environmental impact of systemic pesticides.

Unfortunately, data from literature on pesticide residue levels in guttations are still unreliable, and very limited information on the environmental variable affecting this contamination is available. Moreover, no data regarding the presence of methiocarb and its metabolite in corn guttations are accessible. This gap is of environmental and health concern as methiocarb and its metabolites (in particular methiocarb sulfoxide and the related hydrolysis products) may be toxic also for vertebrates and mammals.

In the present study a LC-HRMS (Q-TOF) methodology has been optimized for the direct determination of methiocarb and its degradation product in guttation drops. The analysis of corn guttations obtained both in field and in greenhouse allowed us to better clarify the metabolic pathway of this insecticide that should be considered in the related environmental risk assessment. In particular, the high concentrations of methiocarb sulfoxide and methiocarb sulfoxide phenol found in guttations confirmed the potential toxicity of drops produced from corn seeds coated with methiocarb.

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## **ANALYTICAL METHODS WITH MINIMAL SAMPLE PRETREATMENT FOR THE CHARACTERISATION OF TRACE COMPOUNDS IN BIOCHAR**

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Biochar is the carbonaceous residue from the pyrolysis of biomass investigated as a soil amendment in agro-environmental practices and waste management. Biochar properties are highly dependent on feedstock /thermochemical conditions. Trace components could be formed during biochar production, retained onto its porous matrix, then potentially released in soil generating beneficial or detrimental effects on biota (e.g. plants, microorganisms) [1]. Despite their importance in field application, the impact of these mobile substances is still unknown due to the lack of analytical investigations. Qualitative assessment of volatile organic compounds (VOCs) was performed by headspace (HS) and gas chromatography-mass spectrometry (GC-MS) [2,3]. Solid-phase microextraction (SPME) is a valid solventless technique for the determination of trace compounds in a variety of matrices, but there are few reports on its application to biochar [4]. Due to its on-fiber pre-concentration capabilities, direct immersion (DI) in water or in head space (HS) are simple approaches for sampling trace compounds trapped in biochar. This study aimed at evaluating HS- and DI-SPME/GC-MS methods for the determination of mobile compounds in biochar. The methods were developed and tested to different biochar types. A variety of compounds including volatile fatty acids, lignin phenols, nitrogen-containing compounds, aromatic hydrocarbons were detected. Due to the limitations of GC-MS for high molecular weight constituents, water extracts were analysed by Fluorescence Excitation-Emission (EEM) Spectrophotometry [5]. The combination of SPME and EEM provided insightful chemical information which may be used to assess the quality of biochar production.

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**DISTRIBUTION OF Cd, Pb AND Cu BETWEEN DISSOLVED FRACTION, INORGANIC PARTICULATE AND PHYTOPLANKTON IN TERRA NOVA BAY (ROSS SEA, ANTARCTICA) DURING AUSTRAL SUMMER 2011-12**

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The aim of this work was to determine the phytoplankton concentrations of Cd, Pb and Cu and to study the influence of phytoplankton on the distribution of these metals in Antarctic seawater. The separation between the algal and the inorganic fractions of the particulate phase let us to better understand heavy metal distribution along the water column. During the XXIX Italian Expedition to Antarctica (austral Summer 2011-2012) three seawater samples were collected in the Ross Sea area near the Italian Station “Mario Zucchelli”. Seawater was sampled by 20-L GO-FLO bottles at three different depths: 5 m, maximum fluorescence depth (between 8 and 15 m) and 100 m. These samples were divided in various aliquots subjected to different treatments for the determination of the principal metal fractions (total, dissolved, particulate and fraction associated to phytoplankton). The phytoplanktonic fraction was separated from the inorganic particulate by a procedure previously set-up [1,2]. The quali-quantitative analysis of phytoplankton was also carried out showing that the major taxa identified are Bacillariophyceae (Diatoms), Dinophyceae (dinoflagellates), phytoflagellates and a little group of Cyanophyceae. All the samples were subjected to microwave digestion before the metal determination. The determination of Cd, Pb and Cu concentrations in the different seawater fractions was carried out by Square Wave Anodic Stripping Voltammetry (SWASV). Cd and Cu show a like-nutrient behavior with total, dissolved and particulate concentrations influenced by the presence of phytoplankton. On the contrary, lead distribution between different fractions in seawater is related to different inputs and the phytoplankton phase influences only partially the behavior of Pb. Our data highlight the significant influence of the phytoplankton on the distribution of Cd, Pb and Cu in seawater, showing a determinant role in the biogeochemical cycles of these metals.

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**SURFACE CHEMICAL CHARACTERISATION OF ATMOSPHERIC PARTICLES OF DIFFERENT SIZE USING XPS.**

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Surface chemical composition of atmospheric particles plays an important role in determining both the reactivity and the optical properties of particles, thereby influencing its role in climate forcing [1]. Surface composition is strongly depending on the sources/formation processes and on the size of particles. Surface composition is also able to influence the risk for human health. X-ray photoelectron spectroscopy (XPS) could be a suitable technique to simultaneously investigate surface composition of particles and chemical speciation of the main elements: C, S, N. In this work, atmospheric particles have been collected, in size-segregated modality, using a 10-stage MOUDI-II rotating cascade impactor in an urban background site in Southeastern Italy and analysed with XPS. The high resolution XPS spectra allowed to distinguish different organic functional groups (C-C/C=C, -C-O, -C=O/-C(O)N, -C(O)O, CO<sub>3</sub><sup>-</sup>) and to speciate the detectable hetero-elements, sulphur (SO<sub>4</sub><sup>2-</sup>, sulphone and sulphide compounds), nitrogen (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and organic-nitrogen compounds), sodium (Na<sup>+</sup>) and chlorine (Cl) species. Significant differences in particles belonging to accumulation (small particles) and coarse (large particles) modes were observed and correlated with the formation processes and the sources from which particles originated. The O concentrations was inversely correlated with C concentrations, however, the content of oxidized organic carbon was not correlated with O content confirming that the O increment in coarse particles can be attributed to inorganic species (crustal origin). The speciation of N showed ammonium only in the accumulation mode and nitrate only in coarse mode excluding the presence of ammonium nitrate in the area studied. A correlation of Na and Cl was attributed to the marine contribution with an excess of Cl on the surface correlated with the depletion of Cl observed in the bulk of particles. Carbonate was present in the coarse fraction and it was associated with crustal aerosol.

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## **INDIVIDUAL PARTICLE SEM-EDX ANALYSIS: AN INTERESTING ANALYTICAL TOOL FOR PARTICULATE MATTER CHARACTERIZATION**

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Atmospheric aerosols draw more and more attention because of their effects on visibility, the direct and indirect effects on radiative balance and at last, but not at least, on human health. Regarding on, the biological mechanisms are not yet been clarified and especially remains to be defined which parameters are more biologically relevant, for example the size fraction, the number or mass of the particles, the chemical composition.

The use of a scanning electron microscope has permitted the investigation of morphological and chemical parameters of the particles. The simultaneous characterization of both physical-chemical, morphological and dimensional parameters of a complex mixture of organic and inorganic particulate is one of the major aspects for the characterization and identification of emission sources which contribute to the concentration of particulate matter in the atmosphere [1; 2]. The particles collected on filters, used for the sampling of urban air, have a large number of shapes and sizes and their chemical composition is very varied.

Morpho-chemical characterisation of particles was performed by ESEM - EDS microanalysis: 21 chemical parameters (C, O, Na, Mg, Al, Si, P, Cd, Cl, K, Ca, Sn, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb) were determined and 8 morphological parameters (area, aspect ratio, roundness, fractal dimension, box width, box height, perimeter and equivalent spherical diameter - ESD) were measured by Image Pro Analyzer 6.3.

A chemical and morphological characterization of particulate matter belonging to three sites was carried out: an urban site, a rural site and an industrial site. The particles were clustered according to their composition and it has been made then a characterization of the three sites based on distribution of these groups of particles.

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**PARTICULATE MATTER AND DECAY OF MATERIALS:  
DEVELOPMENT OF A METHOD FOR SEM/EDS ANALYSIS OF  
ATMOSPHERIC DEPOSITION SAMPLED THROUGH “DEPOSITION  
BOX”**

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Atmospheric Particulate Matter (PM) can induce aesthetic damage and decay of materials. Studying the effect of dry depositions is really complex, especially regarding artistic and architectural surfaces [1]. Up to now, there are no reliable sampling methods to obtain reproducible PM deposits in terms of mass and of uniformity of coverage, both on real or surrogate surfaces.

In this work, a new type of “deposition box” [2] is used to collect PM directly on marble and aluminum specimens. Several sampling campaigns have been performed at two different sites in the urban area of Milan.

A methodology based on Variable Pressure Scanning Electron Microscopy (VP-SEM) and Energy Dispersive X-ray Spectrometry (EDS) analyses has been set up to characterize the specimens as regards size, shape, distribution and elemental composition of the collected particles, thus providing fundamental information to validate the new sampling system without modifying the specimens nor the deposits. Specifically, through VPSE and QBSD detector, SEM images are acquired at different magnification (100x-5000x) according to a mapping path, in order to represent the whole sample. Then images are processed through the freeware software *ImageJ* to evaluate the size range (from 150  $\mu\text{m}$  to 1  $\mu\text{m}$ ) of the particles and their number as a function of their size. The area of the biggest particle founded is 1081  $\mu\text{m}^2$  and of the smallest one is 0,383  $\mu\text{m}^2$ . The combined elaboration of SEM images and respective EDS maps allow also to determine the covering grade of the specimens, that ranges from 21% to 75%, depending on the material and on the different site and time of exposure.

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**COMPETITIVE ADSORPTION OF ORGANIC POLLUTANTS AND LIGNIN DERIVATIVES PHENOLIC COMPOUNDS ON HYDROPHOBIC ZEOLITES**

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BTEX and chlorinated aromatic hydrocarbons seriously contribute to surface and groundwaters pollution, mainly due to crude oil spill and to leakages from industrial wastewaters [1]. Sorption based technologies were demonstrated to be efficient and economical methods for the removal of these contaminants. Among the large number of inorganic adsorbents, the efficiency of organophilic zeolites for the removal of organic contaminants from dilute aqueous solutions has been proved [2, 3]. Due to their chemical composition and to the possibility to be completely regenerated at low temperatures, zeolites can be considered environmental friendly materials.

In this work, hydrophobic zeolites ZSM-5 and Y, which differ in framework topology and channels system, were tested for the adsorption of aromatic hydrocarbons (toluene and chlorobenzene) and the results revealed high saturation capacities and fast kinetics. Since the presence of natural organic matter (NOM) can affect organic pollutants adsorption, the effect of lignin derivatives phenolic compounds on the adsorption properties was investigated. Molecular dimensions of the selected NOM monomers (caffeic acid and para-hydroxybenzaldehyde) are smaller than adsorbent pores size and similar to that of organic pollutants. Consequently, the phenolic compounds can be hosted into the zeolite frameworks. Experimental results, indeed, confirm that both caffeic acid and para-hydroxybenzaldehyde are highly adsorbed on zeolites. However, competitive adsorption of mixtures of organic pollutant and NOM monomer on zeolites shows that aromatic hydrocarbons are preferentially adsorbed. The selectivity and efficiency of the selected zeolites towards organic pollutants in presence of NOM make these adsorbents promising in remediation technologies of natural waters.

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**THE IMPACT OF SHIP TRAFFIC AND HARBOUR ACTIVITIES ON AIR QUALITY: THE CASE OF VENICE**

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Harbours are important hubs for economic growth in both tourism and commercial activities. They are also an environmental burden being a source of atmospheric pollution often localized near cities and industrial complexes. This is particularly true considering that, at global level, landbased emissions of airborne pollutants are decreasing, but ship emissions are increasing leading to potential negative effects on health and climate and social welfare [1]. The aim of the POSEIDON project (POLLution monitoring of Ship Emission: an Integrated approach fOr harbor of the Adriatic basiN) is to quantify the relative contribution of maritime traffic and harbor activities to atmospheric pollutants concentration in four port-cities of the Adriatic Sea (Brindisi, Venice, Patras and Rijeka). This study focuses on the port-city of Venice. The ship traffic impact was quantified on various pollutants: i) gaseous and particulate PAHs; ii) metals iii) PM<sub>10</sub> and PM<sub>2,5</sub>. PAHs were collected in summer 2009 and 2012 using a double sampling method, in order to compare pollutants concentration in dependence of the wind sector where they are coming from [2]. The contribution of ship traffic to metals was evaluated elaborating data collected in a longer period (from 2007 to 2013) using the positive matrix factorization method. In the end the effect of ship traffic to PM<sub>10</sub> and PM<sub>2,5</sub> was calculated applying the equation introduced by Agrawal [3] to the same data. All contributions were correlated with the tonnage of ships during the sampling periods and results were used to evaluate the impact of the European Directive 2005/33/EC on air quality in Venice.

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## A FAST ROUTE TO THE DECONTAMINATION OF MICROWAVE VESSEL FROM CHLORINE SPECIES

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Microwave assisted digestion in closed vessels is a widely employed method for sample preparation in inorganic analysis. Several benefits result from the adoption of closed vessel, microwave assisted dissolution, namely accelerated digestion time, reduced risk of environmental contamination and limitation in volatile analyte loss. Fluopolymers are largely employed as sample holder because of their excellent chemical stability: nevertheless, carryover effects have been evidenced due to the relatively high temperature (typically up to 200°C) and pressure (up to 10 MPa with high pressure modules) reached during the digestion procedure. Permeation of gases into the polymeric matrix has been demonstrated and is the main mechanism responsible for carryover effects: gases enter the voids in the polymeric matrix during microwave digestion (high temperature and pressure) and are trapped inside the polymer when it cools to room temperature. During the following use of the vessels, the entrapped gases are released back into the digestion vessel, leading to the contamination of the attack mixture by gaseous species formed during the previous digestion. The interest focused on the release of chlorine containing species after digestion with *aqua regia*, as they cause deleterious effect on the determination of silver and other elements (mainly mercury(I) and, to a lesser extent, lead) which form sparingly soluble chlorides. Two strategies may be adopted to get rid of this contamination, namely extensive cleaning by repeated treatment with acid mixtures, not including the contamination source, or a thermal treatment of the vessels at 140°C under vacuum for 17 hours. Both techniques show several drawbacks, the most relevant being the time required to decontaminate the vessels.

Aim of the present work is to identify the chloride species responsible for the contamination of the vessel inner surfaces and, based on this information, setup a faster and effective route to their removal. The research experimentally identified the chlorine species trapped inside the polymeric matrix by mass spectrometry. It was shown that a simple microwave digestion employing hydrazine at pH 12 lead to a satisfactory removal of 99.9% of the contamination by chloride in one hour only.

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## **A 'CLEAN & CHECK' METHOD FOR THE SIMULTANEOUS RECOGNITION OF ALBUMEN AND YOLK BY BIOSENSING: APPLICATION IN CULTURAL HERITAGE CONSERVATION**

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Label free and real time optical transduction, in particular by Surface Plasmon Resonance (SPR), is undoubtedly at the forefront of affinity-based biosensing (1,2) thanks to its sensitivity, specificity, versatility, miniaturization perspectives, reusability, and low cost. Despite its application to a broad area of interests, from environment to food analysis, from drug discovery to diagnostics, their exploitation in cultural heritage conservation is still unexplored. Water-based Highly Viscous Polymeric Dispersions (HVPD) composed by polyvinyl acetate (PVA), borax, and water, were recently developed and successfully exploited for the selective removal of protein materials from painted surfaces of historical and artistic interest (3,4). This cleaning method is here coupled for the first time to a SPR biosensor to simultaneously recognize albumen and/or yolk in HVPD extracts. As specific biomarkers, ovalbumin and immunoglobulin Y are selected for egg white and yolk recognition, respectively. The corresponding antibodies were covalently immobilized on carboxymethylated chips for SPR and exploited as bioreceptors. The biosensor was first characterized with reference standards in terms of reproducibility, sensitivity, and selectivity. Then, a combined 'clean & check' approach was optimized, consisting in the HVPD application on simulated and real art samples followed by the evaluation of hen egg presence in the extract, i.e. albumen, yolk, or their co-presence in the matrix. The method is mini-invasive and fast, allowing also the further identification of other protein matrices possibly present in the HVPD extract.

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**APULIAN RED FIGURED POTTERY FROM TARANTO (SOUTHERN ITALY). NON LINEAR STATISTICAL METHOD TO CAPITALIZE CHEMICAL DATA IN ARCHAEOOMETRY.**

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Statistical techniques, when applied to data obtained by chemical analyses on ancient ceramic, are usually expected to identify groups of objects, to classify the finds, to attribute the provenance of items compared with earlier investigated ones or to determine whether an attribution is possible or not. The statistical technique most frequently used in archaeometry is the Principal Components Analysis (PCA), however, its use in archaeometry showed limitations due to its linear feature. Therefore, our aim is testing a different statistical technique for archaeometry. We propose a nonlinear PCA (NLPCA) method, to extract maximum chemical information by plotting data on the smallest number of principal components to answer archaeological questions. The more accuracy and effectiveness of NLPCA approach with respect to standard PCA for the analysis of archaeometric data is pointed by the study of Apulian red figured pottery (V-IV century BC) coming from Taranto (Italy). The results obtained from the treatment of compositional data, combined with those driven from mineralogical composition of pastes – obtained by Optical and Electron Microscopy with Energy Dispersive X-ray Spectroscopy and X-ray Powder Diffraction-, allow to formulate hypotheses about the provenance of the objects, the manufacturing tradition of the workshops and the existence of cultural exchanges. It is worth noting that the statistical approach here proposed made possible a better understanding of the relationship among ceramic technology, artistic expression and workshop practice in the analyzed samples. Several analytical techniques were used to investigate items.

The results achieved showed the adequacy of this statistical treatment for the treatment of archaeometric data as well as it answered archaeological questions.

**OILS USED IN MODERN OIL-BASED PAINT MEDIA: A COMPREHENSIVE STUDY BY MASS SPECTROMETRY**

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Vegetable oils used as artists' materials consist of mixtures of triacylglycerols (TAGs), glycerol tri-esters of fatty acids. In recent years paint manufacturers exploited new vegetable oils as paint binders, to partially replace traditional drying oils (linseed, walnut and poppyseed oils). Although linseed oil is still frequently used in paint industry, walnut and poppyseed oils are rarely employed today. Other oils such as sunflower, safflower, soy, castor, coconut, cotton, oiticica, peanut, rapeseed, tall and tung, sometimes mixed together, have been introduced in the production of modern paint tubes since the beginning of the XX century.

Although paint oils were and still are widely used by contemporary and modern artists, there is a general lack of knowledge on their behaviour upon curing and ageing. Thus, the aim of the present work is the characterization of these new binding media and the study of their ageing pathways.

Traditionally, the analysis of lipid binders has relied on the evaluation of characteristic ratio values of fatty acids amounts by gas chromatography/ mass spectrometry (GC/MS). In this study, we applied high-performance liquid chromatography (RP-HPLC) coupled with high-resolution tandem mass spectrometry (HPLC-ESI-Q-ToF) for comprehensive TAGs analysis. We took into consideration several oils used by paint manufacturers in modern oil paints: linseed, safflower, soybean, sunflower, tung, palm and castor oils. Both natural and artificial ageing experiments were carried out to study the curing and degradation processes. The fresh and aged oils were characterized by GC/MS to obtain their fatty acids profile. The same samples were analysed by HPLC-ESI-Q-ToF. The changes in the profiles of the six oils were interpreted and discussed.

Moreover, the multi-analytical approach based on mass spectrometry was used for the study of original paint materials from Munch's atelier (Munch Museum, Oslo). The results obtained in the analysis of paint tubes were compared with those achieved for a paint sample collected from one of the artist's sketches for the decoration of the Festival Hall of the University of Oslo (1909-1916). The combination of the data obtained by these complementary techniques highlighted the differences between the binding media produced by different manufacturers, permitting to identify the natural sources used to manufacture the paints, and gave us new insights on conservation issues.

## DETECTING DYES ON MICRO-SAMPLES FROM THE CULTURAL HERITAGE - A CHALLENGE FOR SURFACE ENHANCED RAMAN SPECTROSCOPY

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Samples from the cultural heritage normally represent intriguing tasks for the analysts, as the most exhaustive information must be obtained from micro-samples from precious objects. Surface Enhanced Raman Spectroscopy (SERS) is a promising technique for such samples, as it enables highly sensitive detection of low concentration analytes.

During the last decades, a number of application of SERS in chemical, material, life and heritage sciences are reported [1]. As for samples from cultural heritage, *ad-hoc* procedures have been exploited for the detection of dyes, as the noble metal substrate highly enhances the Raman signals while quenching fluorescence [2].

*In-situ* extractionless SERS with silver nanoparticles was successfully employed for the detection of dyes in swatches by Mariano Fortuny [3] and a similar approach was employed to elucidate the composition of lake pigments in cross sections [4].

In our experience this methods fails in producing a rapid response for archaeological samples such as red Egyptian textiles from Pharaonic and Byzantine periods. The topic was faced here by modifying the plasmonic substrate in order to break the bond between the dye and the mordant ions, thus pushing its interaction with the plasmonic substrate. Another intriguing task is SERS investigation of “purple codices”, which are among the most prestigious artworks of Medieval age. The possible use of a mixture of two colorants (i.e. orchil and folium) has been hypothesized. Investigations on model samples highlighted a competitive effect that may affect the results obtained by SERS.

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**MOLECULAR TRACERS OF HUMAN SETTLEMENT AND AGRICULTURAL ACTIVITY IN SEDIMENTARY RECORDS**

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Lacustrine sediments constitute a highly informative environmental archive, due to the large number of biomarkers that can be used for paleoclimatic reconstructions over long time intervals, especially by using a multi-proxy approach. Some organic biomarkers can provide information on the history of human activities and their influence on past climate. The spread of agriculture and pastoralism, including forest clearance activities operated on a large scale through controlled fires, resulted in huge changes in land use, recorded in sedimentary archives. Biomarkers employed as tracers for biomass burning and human/livestock presence include levoglucosan and some specific faecal sterols [1], respectively.

However, the complexity of the matrix and the presence of several possible interferences require high analytical performance and a considerable effort in sample preparation and method development. In this work, a Gas Chromatography – Mass Spectrometry (GC-MS) and Ionic Chromatography – Mass Spectrometry (IC-MS) method based on Accelerated Solvent Extraction (ASE) of lacustrine sediments was developed and validated. Extraction was performed using a DCM:MeOH 9:1 v/v mixture. Extracts underwent clean-up by means of 2 g SPE silica tubes, collecting two different fractions for faecal sterols and levoglucosan then subsequently analyzed with GC-MS and IC-MS [2], respectively.

The method was applied to a 360 cm core retrieved from Lake Trasimeno (Italy), divided into 72 subsamples and covering the last 25 ky. Results were interpreted according to the age model and the available historical information.

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[2] T. Kirchgeorg, S. Schüpbach, N. Kehrwald, D.B. McWethy, C. Barbante, *Organic Geochemistry* 71 (2014) 1-6

**FURTHER THERMAL ANALYTICAL AND CHEMOMETRIC TESTS ON HUMAN FOSSIL BONES FROM TWO NECROPOLISES IN NORTHERN SUDAN**

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The dating of bone finds can be of great use in archaeological and anthropological studies currently carried out in ancient graveyard sites, for instance in Northern Sudan. Notably methods such as the carbon 14 method can satisfy this need. However this method is costly and time-consuming which hinders its application to a wide range of finds, something the above researchers would like. For this reason, in recent years, our research team, which has considerable experience in both thermal analytical and chemometric methods, has investigated the possibility of obtaining data much more rapidly concerning the age of fossil human bone samples by means of thermogravimetric analysis (TG, DTG), supplemented by chemometric processing of the thermal analytical data obtained. To this end, in previous research [1], although still not able to construct actual archaeometric curves, it was possible to demonstrate that it is certainly possible to split into two separate clusters very ancient samples, for instance mesolithic or neolithic specimens, on the one hand, and less ancient specimens, dating to several hundreds of years before or after the birth of Christ, on the other. In the research previously published by us [1], carried out on samples from the aforesaid Sudanese graveyards it was possible to divide the finds into two quite separate clusters above all on the strength of the percentage collagen and carbonates they contained as determined by thermogravimetric analysis. However, one point pertaining to our previous research remained unsettled. This involved the remarks made by several authors who, although agreeing with our results concerning fossil samples from each of the two clusters, nevertheless attributed the differences, at least in part, to differences in the type of bone taken from different anatomic portions of the skeleton. The results of principal components analysis obtained in the present research has enabled it to be concluded, with regard to what was left undetermined in the previous article [1], that the part of the anatomy from which the bone is taken has much less importance than the age of the sample of skeleton being tested. The different anatomic origin of the bones does not seem to have a very important effect, particularly in the more ancient, and thus more highly mineralized, bone samples.

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**RATIONAL DESIGN OF pH-CONTROLLED DNA STRAND DISPLACEMENT**

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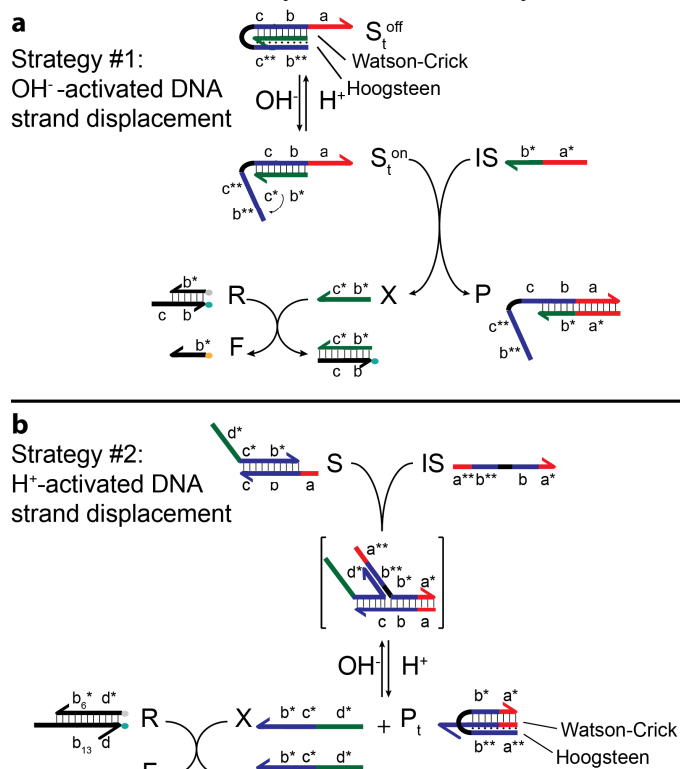
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Achieving strategies to finely regulate with biological inputs the formation and functionality of DNA-based nanoarchitectures and nanomachines is essential towards a full realization of the potential of DNA nanotechnology. We demonstrated an unprecedented, rational approach to achieve control, through a simple change of the solution's pH, over an important class of DNA association-based reactions. To do so we took advantage of the pH-dependence of parallel Hoogsteen interactions and rationally designed two triplex-based DNA strand displacement strategies that can be triggered and finely regulated at either basic or acidic pHs. Because pH change represents an important input both in healthy and pathological biological pathways, our findings can have implication for the development of DNA nanostructures whose assembly and functionality can be triggered in the presence of specific biological targets.

More specifically, we designed two complementary strategies, for which DNA-strand displacement is activated either at basic pHs (strategy #1) or at acidic/neutral pHs (strategy #2).

Triplex formation in both the strategies allows to rationally control the displacement process by simply changing the solution's pH. For example, for strategy#1, at pH 8 (a pH at which triplex formation is unfavoured), strand displacement proceeds with a fast kinetic upon invading strand (IS) addition. At pH 5, in contrast, which is acidic enough for the clamp-like strand to form a triplex inactive



complex, the addition of the IS does not result in any significant signal change, suggesting that no displacement occurs.

In the second strategy developed, pH-dependent triplex formation triggers strand displacement. At pH 8, the addition of the IS does not result in any significant fluorescence signal increase. In contrast, at pH 7, the addition of the IS successfully leads to the strand displacement reaction. In this H<sup>+</sup>-activated strategy, a pH change of just one unit (from pH 8 to pH 7) is sufficient to activate/inhibit the strand displacement process and similarly to what we have achieved with the OH<sup>-</sup>-activated strategy.

The possibility to activate/inhibit the toehold-exchange DNA strand displacement process through a simple change of the solution's pH appears particularly interesting for several reasons. For example, our approach would permit in principle to regulate DNA-based origami formation or DNA-based nanodevices' activity exclusively through pH changes. In addition, since pH dysregulation is often associated with different diseases [1], it could be useful to activate the functionality of drug-releasing DNA-based nanomachines only at specific pH values.

[1] B.A. Webb, M. Chimenti, M.P. Jacobson, D. L. Barber, *Nat Rev Cancer* 2011, *11*, 671

**POST-TRANSLATIONAL MODIFICATIONS: DEVELOPMENT OF NEW MATERIALS FOR THE ENRICHMENT OF PHOSHOPEPTIDES**

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Protein phosphorylation is one of the most important mechanisms to regulate cellular processes. Mass spectrometry is currently the method of choice to detect changes in protein phosphorylation. However, the identification of phosphorylation sites is challenging, due to the low abundance of phosphorylated proteins in eukaryotic cells. In this regard, highly sensitive methods and enrichment strategies selective for phosphopeptides are necessary. Current enrichment strategies basically rely on affinity chromatography, but they still do not provide complete coverage of the phosphoproteome in complex systems [1]. In this context, the general aim of this work was to develop innovative and alternative materials for the highly selective enrichment of phosphopeptides. In particular the attention was focused on perovskites, such as  $\text{CaTiO}_3$  and  $\text{CaMoO}_4$ , which were initially compared to the most frequently employed stationary phases based on  $\text{TiO}_2$ , for the enrichment of phosphopeptides using a microcolumn format. The protocol was first developed on simple tryptic mixtures, starting from casein digests, then the new stationary phases were used to enrich phosphopeptides from increasingly more complicated mixtures (such as casein and bovine serum albumin in different ratios), aiming to apply the optimized protocol to real complex samples. The investigation of the microcolumn performance was characterized by strict analytical methods, also employing phosphopeptide standards to calculate recoveries and matrix effects, which are usually neglected in material development for phosphopeptide enrichment. In parallel to the investigation of new stationary phases for microcolumn devices, alternative systems were also developed to simplify the enrichment procedure; in this sense core-shell magnetic beads were considered, due to the ease of use of such devices with respect to microcolumns. To modify the surface of the  $\text{Fe}_3\text{O}_4$  magnetic beads we employed dopamine, which is able to spontaneously polymerize in mild conditions to form polydopamine, a versatile biocompatible polymer, which in turn is suitable to anchor metal cations, such as  $\text{Ti}^{4+}$ . The enrichment performance and the identification of enriched phosphopeptides with the various developed stationary phases was assessed by nanoHPLC-MS/MS analysis and shotgun proteomics.

[1] J. D. Dunn et al. *Mass Spectrometry Reviews*, 29 (2010) 29–54

## A FLUORESCENT IMMUNOCHROMATOGRAPHIC STRIP TEST USING QUANTUM DOTS FOR FUMONISINS DETECTION

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Rapid diagnostic assays have been in use for decades in the clinical and medical sector. Nowadays rapid immunoassay-based tests are widely applied in clinical, drug, food and environmental analysis. The immunochromatographic strip test (ICST), also known as lateral flow immunoassay, offers many advantages when compared to other immunoassay methods such as user-friendly format, rapid detection (results usually come within 10–20 min), no requirement of equipment or technical expertise and relatively low cost. ICST devices involve immunoassays in which the sample flows by capillary forces along an analytical membrane that contains immobilized immunoreagents.

Traditional ICSTs employ colloidal gold to generate visual signals and usually provide a binary yes/no answer. However, to reach better sensitivity and easier objective interpretation, new labels need to be explored. Different analytical methods have shown that the use of fluorescent than colorimetric labels leads to a significant lowering of the detection limit, so fluorescent materials represent an obvious first choice. Fluorescent semiconductor nanocrystals (Quantum Dots, QDs) are among the most promising labels for ICT. Compared to conventional fluorophores, QDs have excellent fluorescent properties, such as high quantum yields, size-tunable fluorescence and broad absorption spectra, narrow and symmetric emission spectra, large molar extinction coefficients, strong fluorescence intensity, and high resistance to photobleaching. Nevertheless, very limited research on competitive QD-based ICST has been reported in the literature [1,2].

In this communication, the QDs usage as labels for the development of a fluorescent ICST will be discussed and demonstrated in a model device to detect fumonisins (FMs) in maize. FMs are mycotoxins mainly produced by *Fusarium* species, whose contamination involves primarily maize. Due to adverse effects in animals and humans, and incidence of FMs, they are regulated by European Union and their monitoring is compulsory for food safety assessment.

[1] A.N. Berlina, N.A. Taranova, A.V. Zherdev, Y.Y. Vengerov, B.B. Dzantiev, *Anal. Bioanal. Chem.* 405 (2013) 4997-5000.

[2] N.A. Taranova, A.N. Berlina, A.V. Zherdev, B.B. Dzantiev, *Biosensors and Bioelectronics* 63 (2015) 255-261.

**THERMOCHEMILUMINESCENT REAGENTLESS ULTRASENSITIVE IMMUNOSENSOR USING ORGANICALLY MODIFIED SILICA NANOPARTICLES DOPED WITH NEW 1,2-DIOXETANE ANALOGUES AS LABELS IN A MINIATURIZED FORMAT**

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We recently demonstrated that thermochemiluminescence (TCL), i.e., the light emission originating from a product in a singlet excited state after the thermolysis of a 1,2-dioxetane derivative, is a powerful tool for new generation of immunoassays, being a reagentless chemical luminescence-based detection technique, thus simplifying the microfluidic network in miniaturized analytical device formats. We overcome the main problems reported for TCL in the past, i.e., the high operating temperature (200–250 °C) and the lower detectability due to the poor fluorescence efficiency of the emitter, by synthesizing a library of new 1,2-dioxetane analogues, proposed as new TCL labels [1-3], characterized by lower emission triggering temperature (80–100 °C) and higher fluorescence quantum yields (0.1–0.5).

A further increased detectability was achieved by light emission amplification by preparing organically modified silica nanoparticles (ORMOSIL NPs) doped with the TCL molecules, which were functionalized with biotin for binding to streptavidin-labeled species, to be used as universal detection reagents for immunoassays. One molecule of protein will be labeled with the functionalized doped nanoparticles, achieving an amplification of 1-2 decades of measured photons. A non-competitive immunoassay for streptavidin (SA) and a competitive immunoassay for valproic acid (VPA) were developed using an analytical format comprising a compact 3D-printed device including a cooled CCD and a miniaturized heater pad encased in kapton, obtaining analytical performances similar to CL detection using horseradish peroxidase (HRP) as label [4].

More recently, we designed a smartphone-based TCL device that is under investigation to develop a TCL-based immunoassay and new TCL molecules have been synthesized and photophysically characterized to obtain even more efficient probes.

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[2] M. Di Fusco, A. Quintavalla, C. Trombini, M. Lombardo, A. Roda, M. Guardigli, M. Mirasoli, *J. Org. Chem.* 78 (2013) 11238-11246.

- [3] M. Di Fusco, M. Guardigli, M. Lombardo, M. Mirasoli, A. Quintavalla, A. Roda, C. Trombini, Patent WO2014024106 A1 (2014).
- [4] M. Di Fusco, A. Quintavalla, M. Lombardo, M. Guardigli, M. Mirasoli, C. Trombini, A. Roda, *Anal. Bioanal. Chem.* 407 (2015) 1567-1576.



## **ICP-MS DETERMINATION OF THE METALLOME OF HUMAN PLACENTA IN GESTATIONAL DIABETES MELLITUS**

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The knowledge of the "omics" and therefore also of the metallomics of Gestational Diabetes Mellitus (GDM) appears to be a necessary task in order to gain information about the molecular causes of this disease. In this work, the metallome of GDM and of other types of diabetes mellitus was reviewed at first. The comparative analysis of the published data revealed that no GDM elemental markers could be identified with sufficient reliability in blood and in the other considered samples, with the partial exception of Selenium. Placenta was chosen as an alternative target organ for the analysis of the GDM metallome. The full elemental average composition of 19 healthy placentas was obtained by ICP-MS. If the median concentration values are considered, the placenta elements can be classified into seven groups, ordered from the most concentrated (C, Ca, H, K, N, Na, and P) to those detected at ppb concentration values (As, Cd, Co, Cs, Hg, lanthanides, Mo, Sc, Sn, and V). Analyses were then performed on 28 placentas of women affected by GDM. The statistical tests and the principal component analysis evidenced that the concentration of most elements was statistically equivalent in healthy and GDM women, with the exception of Cd and Se: Cadmium had lower concentrations, and Selenium had higher concentrations, in GDM placentas than in the control group. These results were interpreted on the light of literature data, and they put the attention on two key elements for the understanding of the GDM molecular pathways.

**LARGE AND FAST QUANTITATION OF PROTEINS WITH SWATH-MS  
IN A KNOCKDOWN CELL LINE**

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The aim of this research was the relative quantitation of the proteome of the murine hepatic cell line AML-12 in which Eukaryotic Initiation Factor 6 (eIF6) was down-regulated by using shRNA. eIF6 is a human gene which is necessary for the 60S ribosome biogenesis and can also acts in the cytoplasm as a translation factor. This gene is crucial for tissue-specific growth and oncogene-driven transformation, and could be a new rate-limiting step for the initiation of translation. The relative quantitation of proteins was performed in wild type (wt) and eIF6sh cells by using the SWATH-MS (Sequential Window Acquisition of all Theoretical fragment ion spectra) analysis which is an high throughput label-free method for protein quantitation that combines the traditional shotgun proteomics with the quantitative accuracy and reproducibility of selected reaction monitoring (SRM). This recent analytical technique is a data independent acquisition (DIA) method that allows a complete and permanent recording of all fragment ions of the detectable peptide precursors present in a biological sample. The analysis was conducted in SWATH-MS acquisition mode on the 5600+ TripleTOF (ABSciex, Concord, Canada) coupled to an Eksigent microLC system (Eksigent, Dublin, Ireland) with a C18 reverse phase column. This proteomic screening of ctrl vs eIF6sh allowed the identification and quantification of tens of modulated proteins in a single experiment.

The consistent and reproducible quantification of proteins by SWATH-MS provides insight into dynamic protein changes following eIF6 knockdown.

**NEEDLE TRAP MICRO-EXTRACTION: A NEW STRATEGY FOR THE COLLECTION AND PRE-CONCENTRATION OF BREATH SAMPLES**

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The chemical characterization of volatile compounds in human breath is a potential tool for modern medicine to obtain clinically relevant information on ongoing body physiological processes in a non-invasive way. Pre-concentration is the crucial step when volatile organic compounds (VOCs) occurring at concentrations in the ppbv or pptv range have to be determined. The needle trap devices (NTDs), i.e. stainless steel needles (internal diameter 0.22  $\mu\text{m}$  and length 6 cm) packed with suitable sorbent materials, represent a new promising tool for a robust and reproducible sample preparation since they combine the advantages of SPE (active adsorption) and SPME (small volume, direct injection in the GC injector) [1].

In this work, the needle trap micro-extraction technique was optimized for the simultaneous collection and pre-concentration of VOCs in exhaled breath. In particular, the effect of different packing materials on the efficacy and reproducibility of VOCs analysis was investigated. Double and triple bed NTDs packed with different combinations of sorbents (e.g. DVB, PDMS, Carboxene X and Carboxene 1000) were tested to evaluate the influence of sampling parameters such as flow rate and sample volume on the adsorption process, as well as the effect of different GC inlet temperatures onto the analyte desorption from NTDs. Particular attention was paid to the use of an internal standard for the normalization of data. All the tests were carried out using a humid standard gaseous mixture composed by 18 VOCs with different chemical and physical properties.

Needle trap devices were automatically desorbed by a CONCEPT NT-sampler and VOCs were detected by an Agilent 7010 Series Triple Quadrupole GC/MS. Detection limits in the range of pptv and ppbv for all the investigated compounds were observed.

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**FUNCTIONALIZED TiO<sub>2</sub> NANOPARTICLES AS ENZYME-LIKE LABELS FOR IMMUNOASSAY**

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Nowadays immunoassays are widely used for bioanalytical applications such as clinical, environmental and food analysis. Generally, these systems are based on a specific antigen-antibody reaction and they use enzymes as labels, such as the peroxidase one. However, enzymes have some drawbacks, i.e. their stability is strongly dependent from analysis conditions as pH and temperature and their preparation and purification procedures could be expensive. Oxide-based nanoparticles present some advantages such as low-cost synthesis, high stability and versatility. Several materials show a peroxidase-like activity and they are already applied in immunoassay both as electrochemical biosensor and colorimetric methods. Here we propose the use of TiO<sub>2</sub>, a widely used photocatalyst, as label instead of peroxidase enzyme.

We conjugated TiO<sub>2</sub> nanoparticles to human serum albumin (HSA), which is important, for example, for diabetes diagnosis, in order to exploit the photocatalytic activity of TiO<sub>2</sub> for enzyme-linked immunosorbent assay (ELISA). TiO<sub>2</sub> particles were produced via hydrothermal synthesis starting from titanium isopropoxide mixed with acetic acid. Titania particles were silanized to perform the conjugation with HSA by using 3-aminopropyl-triethoxysilane for silanization. Preliminary, we functionalized TiO<sub>2</sub> particles with BSA (TiO<sub>2</sub>-BSA) and we investigated the peroxidase-like activity under UV irradiation by using 3,3',5,5'-tetramethylbenzidine (TMB) with hydrogen peroxide as substrate. We optimized the analytical system by studying the influence of different parameters, i.e. ratio between TMB and H<sub>2</sub>O<sub>2</sub>, temperature, pH and irradiation time on the assay. We investigated the applicability of TiO<sub>2</sub>-BSA as a tracer in a direct competitive immunoassay for the detection of BSA by studying the binding between immobilized antibodies and TiO<sub>2</sub>-BSA. We demonstrated that the TiO<sub>2</sub> probe permits the measurement of antigen-antibody complex formation and the establishment of an immunoanalytical test similarly to enzymatic probes. Then, we tested the system to the analysis of HSA. We demonstrated that HSA labelled with TiO<sub>2</sub> could be effectively used in a competitive immunoassay for measuring HSA.

**DYNAMICS OF SILVER NANOPARTICLES IN HUMAN SKIN *IN VIVO* STUDIED BY SYNCHROTRON RADIATION AND ICP-MS**

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The topical application of silver nanoparticles (AgNPs) is increasingly used in the treatment of burns to prevent infections and favour the regeneration of the tissue. We have shown that AgNPs can penetrate into the dermis, are taken up by the fibroblasts and interact with mitochondria,<sup>1-3</sup> but no data are currently available on their subsequent chemical transformations, which are key processes to determine their potential toxicity.

Here, we present the first high resolution spatial and temporal data on silver distribution and speciation in depth profiles of burned skin after application of AgNPs. Full-profile biopsies of the wound were collected from a patient before treatment, and then at 3-days intervals up to the complete healing. Elemental imaging maps and speciation were obtained using synchrotron radiation  $\mu$ XRF and  $\mu$ XANES on selected slices from each biopsy, and allowed to elucidate the chemical transformations and penetration of AgNPs into the tissue. The potential of AgNPs to reach the systemic circulation was investigated by developing a new analytical method for the simultaneous determination of dissolved Ag and characterization of AgNPs in human blood, based on hydrodynamic chromatography hyphenated to single-particle ICP-MS, and combined with a new ad-hoc algorithm for data treatment. Within a single analytical run, the method provides the deconvoluted chromatogram and concentration of dissolved Ag species, and the multidimensional distribution of AgNPs in terms of hydrodynamic diameter, mass-derived diameter, size-dependent number and mass concentrations, total number and mass concentration. The method was applied to study the dynamics of AgNPs in human plasma *in vitro*, and to investigate the presence of AgNPs in the blood of three burnt patients.

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## ULTRASENSITIVE LATERALFLOW IMMUNOASSAY WITH CHEMILUMINESCENT DETECTION: NEW MINIATURIZED AND SMARTPHONE-BASED DEVICE

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Lateral Flow Immunoassay (LFIA) is a technology currently widely applied in resource-poor or non-laboratory environments (point-of-use) that is based on prefabricated strips of a carrier material containing dry reagents that are activated by applying the fluid sample. The conventional LFIA are available mostly for qualitative analyses, but using enzymes as tracers, coupled with chemiluminescence (CL) detection, it is possible to obtain quantitative information and reach high detectability [1].

Here, we report about the latest advances in CL-LFIA based technologies. We have developed a simple, rapid and accurate biosensor based on CL-LFIA and a smartphone camera as light detector [2]. Nowadays the improved image-processing technology of the back side illuminated CMOS sensors used in smartphone cameras make them suitable for fast and accurate point-of-care diagnosis based on CL-LFIA [3,4]. These kind of biosensors will be useful in all situations where a decentralized and fast detection is required taking advantages of the connectivity, location (GPS), long distance transfer of data via wireless. Using a 3D printer, we made simple accessories (a cartridge, which houses the LFIA strip, and a smartphone adaptor) to turn a smartphone into a biosensing device for the quantification of salivary cortisol. Now we are exploiting the simplicity and portability of the CL-LFIA based device in order to develop a biosensor for the quantification of salivary biomarker that will be used by crew members aboard the International Space Station. The self-standing device will be composed by a cartridge that contains all the reagents necessary for the immunoassay and it will integrate all the microfluidic elements.

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**RECENT ADVANCES IN CONSENSUS MODELLING OF MULTIPLE ANALYTICAL CHEMICAL DATA**

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Recent advances in technology enabled the collection of huge amounts of data from multiple analytical sources. Data fusion jointly analyses data achieved by means of a variety of analytical techniques since their combination can enhance the identification of relevant information in the analytical data.

An alternative to directly merge all available analytical sources is the so called consensus approach, which was introduced for Quantitative Structure Analysis Relationship (QSAR) models. Consensus analysis combines predictions obtained by different modeling techniques. It is demonstrated that this approach can improve the quality of predictions and diminish the effects of noisy data by averaging the predictions of several models [2].

This presentation deals with the application of consensus approach on real analytical data of food samples with different geographical origins derived from several analytical techniques. The aim is to show how recent advances in consensus modelling, such as the application of Dempster-Shafer theory of evidence and Bayesian approaches, can reduce uncertainty in analytical data with conflicting information, enhance data interpretation and benefit from all sources of information without compromising the quality of analytical model predictions.

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**SPARSE METHODS APPLIED TO HYPERSPECTRAL IMAGING:  
CLASSIFICATION OF ARABICA AND ROBUSTA GREEN COFFEE  
BEANS**

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In the present work, sparse methods are investigated for classification and variable selection of hyperspectral images in order to separate Arabica and Robusta green coffee beans.

The main aspect of sparse methods is the possibility of performing variable selection by forcing to zero the model coefficients related to uninformative or noisy variables. Therefore, sparse methods are extensions of classical calibration or classification methods, in which sparsity is induced on the model parameters by adding a penalty term to the objective function of the considered reference method. In this manner, sparse methods allow to perform either calibration or classification and variable selection at the same time in a one-step automated procedure. The level of sparsity to induce on the model, as well as the number of components, is a user-defined parameter to be tuned on the basis of model performances and stability.

In this study, two different sparse classification approaches, i.e. sPCA+kNN [1] and sPLS-DA [2], were considered and compared both each other and with the corresponding classical (non-sparse) methods. Both algorithms use the Lasso [3] approach to induce sparsity, which essentially consists in adding a L1 norm penalty to the least squares criterion, where the L1 norm is the sum of the absolute values of a vector.

In particular, hyperspectral images of Arabica and Robusta green coffee samples were acquired in the NIR range (955-1700 nm) obtaining images composed by 150 spectral channels. The classification performances of sparse and non-sparse methods were evaluated both at the image-level and at the pixel-level on a test image. In our case, sparse methods gave high classification efficiency values similarly to classical methods, but they allowed to obtain models more interpretable and much more parsimonious.

An important aspect to highlight is that the two different sparse classification approaches converged to the selection of the same spectral regions, which confirms the chemical relevance of the selected wavelengths in the discrimination of Arabica and Robusta green coffee beans.

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**DIFFERENT APPROACHES TO THE ANALYSIS OF DESIGNED NIR FINGERPRINTING DATA**

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The study of treatments effect is a very general issue, which encompasses several research fields from biomedicine, metabolomics to food processing and material science. The main framework is to assess if different treatments (factors), and which, affect the studied system and how. Using Analysis of Variance (ANOVA) has traditionally assessed these questions, however when several parameters are used to characterize the samples groups and, especially in the case of instrumental characterization, it has been demonstrated that coupling ANOVA with multivariate data analysis is far more efficient. In particular, ANOVA Simultaneous Component Analysis (ASCA) and ASCA combined with PARAFAC (PARAFASCA) have been proposed [1-2]. These methods, which are based on fitting a multivariate decomposition model on each ANOVA term, allows for easy interpretation of the variation induced by the different factors of the design due to the graphical representation in components space and projection/evaluation of residuals. In particular, ASCA describes each variance contribution with a PCA model, but a contribution depending on crossed factors (interactions) may be described more parsimoniously by multiway models like parallel factor analysis (PARAFAC). In both cases designed data are described in a way that is both parsimonious and focused on the experimental question.

The study of thermal treatments changes in moderate range of temperatures for spruce wood has been used as benchmark to illustrate the methodology.

According to ISPM-15 standard, all wood materials to be shipped should be heat treated with specific time-temperature schedules. Thus, it is commercially important to have a fast method to estimate if a wood has been treated or not, to this aim Near Infrared Spectroscopy has been used as fingerprinting technique to evaluate if could be sensible to changes to wood chemical/physic structure induced by temperature and exposition time.

Experiments have been planned according to a design taking into account three factors: temperature, treatment time and time occurred from treatment to the measurement.

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**LIMIT OF DETECTION AND QUANTIFICATION IN THE PRESENCE OF INSTRUMENTAL AND NON-INSTRUMENTAL ERRORS: STUDY OF THE POSSIBLE SOURCES OF ERROR AND APPLICATION TO THE ANALYSIS OF AT TRACE LEVELS BY ICP-MS TECHNIQUE**

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The detection limit (LOD) and quantification limit (LOQ) were estimated when signals were affected by two error contributions, namely instrumental errors and operational-non-instrumental errors. The LOD was theoretically obtained following the hypothesis testing schema implemented with the calibration curve methodology. A two-components variance regression was performed to determine the calibration curve and to define the detection limit in these conditions. The detection limit values obtained from the calibration at trace levels of 41 elements by ICP-MS resulted larger than those obtainable from a one component variance regression. The role of the reagent impurities on the instrumental errors was ascertained and taken into account. Environmental pollution was studied as source of non-instrumental errors. The environmental pollution role was evaluated by Principal Component Analysis technique applied to a series of nine calibrations performed in fourteen months. The influence of the seasonality of the environmental pollution on the detection limit was evidenced for many elements usually present in the urban air particulate. The obtained results clearly indicated the need of using the two-components variance regression approach for the calibration of all the elements usually present in the environment at significant concentration levels.

Three LOQ definitions were accounted for. One of them in the concentration and two in the signal domain. The LOQ computed in the concentration domain, proposed by Currie [1], was completed by adding the third order terms in the Taylor expansion because they are of the same order of magnitude of the second ones so that they cannot be neglected. In this context the error propagation was simplified by eliminating the correlation contributions by using independent random variables. Among the signal domain definitions, a particular attention was devoted to the recently proposed approach based on at least one significant digit in the measurement [2].

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**THE COMBINATION OF RAPID ANALYTICAL PROFILING AND DATA FUSION CHEMOMETRIC TOOLS FOR THE IDENTIFICATION OF ADULTERATIONS AND FOR PROVEVANCE STUDIES OF DIFFERENT FOOD MATRICES**

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Official methods for food composition characterization are useful to identify more striking adulterations or bad storage conditions, while they often fail in the identification of product origin and complex adulterations. To satisfy the interest of consumers in the identification of the origin of products or in the identification of food adulterations, many scientific studies have been recently published exploiting different profiling tools (NIR, IR and Raman spectroscopy or electronic nose) [1-5]; however, one single analytical technique at a time is usually exploited.

Here, different profiling methods have been coupled (consisting in IR and NIR spectroscopy, electronic nose profiling, SPME-GC-MS) for the characterization of different food products (honey, balsamic vinegars, grana cheese etc). The results obtained were then coupled to provide an overall description of each sample investigated. Data fusion tools, as Multiple Factor Analysis [6] were then exploited to analyse the results obtained by the different analytical techniques on their whole and improved the classification performance of the models calculated.

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## **VALIDATION: STILL AN UNEXPLORED LAND?**

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In multivariate data analysis, descriptive or qualitative/quantitative models are often built for the sake of interpreting the experimental results or to be able to make predictions on future samples. In this context, whatever the method concerned, no modelling approach should prescind from an estimate of the reliability or the validity of the proposed interpretation or of the resulting predictions; in a single word, from a proper validation. But the concept of validation is even more general, encompassing questions such as whether an appropriate model was chosen, or if outliers and/or highly influential points are present in the data set, or again not only whether the optimal dimensionality was chosen but also if the selected subspace remains stable over different samplings of the same population.

Accordingly, it is of utmost importance that the validation schemes adopted reflect the questions answers are sought for: an improper validation can be even more dangerous than performing no validation at all, if one is deluded to have behaved correctly.

However, despite this key role, still many papers are published and presented, which seem to ignore these fundamental issues, lacking a proper validation strategy or even not considering validation at all. Extreme cases of such a behavior can include situations (reported in the literature) where, for instance, even replicate measurements taken on the same samples are split between training and test sets, not to mention the validation of underlying hypotheses which is often neglected.

In the present communication, these general concepts and the risks associated with an incorrect validation will be illustrated with some real world examples, mostly involving spectroscopic data sets.

**ARRAYS OF HETEROGENEOUS SENSORS, CONTINUOUS MONITORING FOR DETECTION OF OLFACTORY NUISANCE AND SELF ORGANIZING MAPS**

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Odour nuisance associated with atmospheric emissions are in several cases characterized by transient events and by the presence of odorous molecules present at very low concentrations (also ppb v/v or below), above respective odor thresholds and close to analytical sensitivity of common detectors. An analytical approach to tackle this complex characterization issue is based on continuous monitoring by gas sensors or "electronic noses". New multi-sensor system recently available for environmental monitoring, integrate arrays of black carbon-polymer composites, initially proposed by Nate Lewis [1], MOS sensors and PID, and generate profiles (smellprints) of mixtures of odour compounds from ambient air with high temporal frequency. Sensitivity, statistical separation of response patterns and speed of response of different sensors to reference gases need to be considered and optimized. The multiparameter profiles can be referred to the European odour units per cubic meter ( $ou_E/m^3$ ) introduced in the UNI-EN 13725:2004. They can also be associated to speed and direction wind data and to humidity. The rationalization of such amounts of multivariate data collection permits the identification of types of air, classified accordingly to smellprints and direction of origin of the olfactory nuisance. The management of substantial quantities of data from environmental odour monitoring (e.g. more than 8000 smellprints per day) is hardly dealt with the classical techniques of multivariate analysis, but they can be effectively tackled with artificial neural networks known as "self-organizing maps"[2]. Such algorithms allow compression of information, classification, evidence of deviations from analytical usual patterns, and ease of visualization of the acquired information.

The approach is discussed on the base of data from a monitoring station close to an industrial site that hosts multiple odour sources.

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**ACCURATE MASS SCREENING WORKFLOWS FOR THE ANALYSIS OF NOVEL PSYCHOACTIVE SUBSTANCES**

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In forensic toxicology testing labs, workflows are trending. Routinely, labs have been tasked with doing targeted analysis, monitoring samples for a standard list of known drug compounds and quantifying any of those targeted compounds that are found. These days with the emergence of many different novel psychoactive substances (NPS), labs are being faced with the challenge to do more surveillance screening. In this workflow, they are required to explore for any compounds that might be present in their samples without any pre-existing knowledge of what those compounds could be. NPS are structurally and/or pharmacologically related psychoactive drugs. Before or upon emergence, they are not controlled or scheduled and so they can be legally circulated. Some common NPS are derived from the phenethylamine, cathinone („bath salts”) and cannabinoid drug frameworks synthesized in clandestine laboratories and marketed over the internet as „legal highs”. In response to legislative efforts to these NPS a constant cat and mouse scenario is created as new NPS emerge on a monthly basis in order to overcome the drug laws. TripleTOF® technology enables the acquisition of high resolution and accurate mass MS and MS/MS information on all peaks observed in any given sample. These information-rich data files can offer insight into the many drugs and metabolites present in a given sample.

The strength of the workflow lies in the software, where PeakView® software with the MasterView™ add-in enables high throughput data analysis, allowing the information rich data files to be quickly screened for both targeted and non-targeted compounds.

The usual workflow in unknown screening for novel psychoactive substances is to analyze the suspicious offenders, discover the unknowns and then add to the routine analysis of targeted drugs. This technical note describes this workflow starting with the untargeted analysis and adding identified unknowns to the targeted list and the ability to use the TripleTOF® for routine, targeted analysis.

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**RECENT TRENDS IN THE ILLICIT CONSUMPTION OF *CANNABIS* DERIVATIVES: AN ANALYTICAL STUDY ON SEIZED MATERIALS**

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Until about the year 2010 hashish has been the main *Cannabis* derivative available in the black market, since preferred to marijuana for its stronger psychoactive effects, due to higher  $\Delta$ 9-tetrahydrocannabinol ( $\Delta$ 9-THC) content. Moreover, hashish higher specific weight allowed more feasible traffic, smuggling, concealment and storage procedures. These trends in *Cannabis* consumption are recently being reversed in fact, in contrast with what was observed in the past, marijuana appears to be now the most popular product in the illegal market, when taking into account the increasing number and extent of seizures made by law enforcement agencies in EU and USA.

The study reported herein deals with the quali-quantitative analyses performed by the Regional Bureau of Scientific Police of Bologna on seized materials collected in Emilia Romagna over a period of 13 years (2001-2014). This report provides data from 3300 lots (hashish and marijuana) analyzed by gas chromatography-flame ionization detection (GC-FID) and liquid chromatography-mass spectrometry (LC-MS). The data showed an upward trend in the mean  $\Delta$ 9-THC content of all confiscated *Cannabis* preparations.

Comparing the obtained experimental data with those already available in the scientific literature and in the on-line databases, it is noteworthy that in many European and American countries there is a significant increase in marijuana power, expressed as the percentage content of its active ingredients. In particular,  $\Delta$ 9-THC levels in seized marijuana batches have virtually doubled in a decade, reaching concentrations usually higher than 10%. Hashish potencies did not increase consistently during this period.

These high contents in  $\Delta$ 9-THC found in marijuana preparations can be explained by the changes in the techniques of selection and intensive cultivation of *Cannabis* plants, which allow obtaining increasingly powerful species and products.

**COCAINE PROFILING: ATR-FTIR SPECTROSCOPY COUPLED TO CHEMOMETRICS AS A RAPID QUANTIFICATION TOOL**

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Cocaine is the most widely used illicit drug, and its “origin” is always the focus of intense investigation aimed at identifying the trafficking routes. The classification of cocaine seized according to its form (composition, cutting agents) provides useful information to enhance the existence of cocaine illicit networks and supply the police intelligence [1].

Typical cutting agents of cocaine are adulterants as caffeine, anaesthetics such as procaine, lidocaine and phenacetin or stimulant like levamisole [2]. From a forensic point of view, the characterization of cutting agents could represent a crucial step because it can link different seizures of cocaine to one original batch.

In this study, a strategy based on Infrared Spectroscopy with Fourier Transformed and Attenuated Total Reflectance associated with chemometrics (ATR-FTIR) is proposed to identify the chemical “fingerprint” of cocaine samples. To this end, standard mixtures of cocaine and cuttings at different ratios were investigated in order to develop a multivariate classification model to simultaneously predict the composition of the samples and to obtain a profile of adulteration of cocaine seized.

Vibrational spectroscopy allows a comprehensive study of several components of a sample in a single instrument measurement without requiring any pretreatment or physical separation. Moreover it is a non-destructive, high resolution and fast scanning technique.

In addition, the application of a Partial Least Squares Discriminant Analysis (PLS-DA) calibration approach was found to be a useful tool to predict the content of cocaine, caffeine, procaine, lidocaine and phenacetin in drug seizures. The achieved results on real confiscated samples, in cooperation with the Italian scientific police (Carabinieri-RIS) of Rome, allow to consider ATR-FTIR followed to chemometrics as a promising forensic tool in such situations involving profile comparisons and classifications and supporting forensic investigations.

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**INNOVATIVE CHEMOMETRIC INTERPRETATION OF AN EXTENDED STEROIDAL MODULE IN THE ATHLETE BIOLOGICAL PASSPORT**

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The distinction between endogenous (physiologic) production of anabolic androgenic steroids and their exogenous administration is difficult to ascertain. This makes endogenous anabolic androgenic steroids (EAAS) the most misused substances in elite sports. Small changes of EAAS concentrations, induced from the intake of low doses of various EAAS at almost physiological levels, are masked by the wide inter- and intra-individual variability of urinary EAAS values. Recently, WADA introduced into the Athlete Biological Passport (ABP) an adaptive statistical model based on Bayesian inference, to detect abnormal values of selected EAAS: testosterone (T), epitestosterone (E), androsterone (A), etiocholanolone (Etio), 5 $\alpha$ -androstane-3 $\alpha$ ,17 $\beta$ -diol (5 $\alpha$ -diol), 5 $\beta$ -androstane-3 $\alpha$ ,17 $\beta$ -diol (5 $\beta$ -diol), and EAAS ratios: T/E, A/T, A/Etio, 5 $\alpha$ -diol/5 $\beta$ -diol and 5 $\alpha$ -diol/E.

Our aims were (i) to develop analytical methods addressed to quantify a wide range of endogenous steroids in urine, and (ii) to develop and compare various multivariate statistical approaches based on effective combination of EAAS values and their ratios, in order to enhance the detection of alleged EAAS misuse by means of the Athlete Biological Passport (ABP).

Urine samples were taken from 108 subjects, including 12 patients under treatment with EAAS. A fully-validated GC-MS method was developed to detect all EAAS recommended by WADA plus several further EAAS reported in literature as potential misuse markers. The experimental data were evaluated by means of three multivariate data analysis techniques, namely Principal Component Analysis (PCA), Unequal Dispersed Classes (UNEQ) and Partial Least Squares Discriminant Analysis (PLS-DA).

Had the standard screening criteria proposed by WADA been used, all 12 positive urine samples taken from subjects assuming EAAS would be classified as negative. Conversely, the application of multivariate statistics allowed us to correctly detect EAAS intake and exclude these samples from the "negative" population. PLS-DA proved to be particularly efficient, showing both sensitivity and specificity equal to 100%. In conclusion, the application of multivariate chemometrics must be introduced into the Athlete Biological Passport in order to assist the correct classification of steroidal profiles, whenever an estimated multivariate threshold is exceeded.

**ARRAYS OF COPPER NANOWIRE ELECTRODES FOR THE SENSITIVE ELECTROANALYSIS OF NITRATE**

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Major anthropogenic sources of nitrate in food and the environment are associated to inorganic fertilizers, food preservatives and other chemicals. Toxicity of nitrate to humans is related to its ability to oxidize hemoglobin (Hb) to methemoglobin (metHb). Nitrate can also act as precursor of nitrite whose carcinogenic or congenital malformation effects are known. The limit of concentration for nitrate in drinking water indicated by the World Health Organization (WHO) is 50 mg L<sup>-1</sup> (10 mg L<sup>-1</sup> for newborns) [1].

Among the analytical methods suitable to determine nitrate, electrochemical ones are very attractive since they are suitable for in-field and decentralized monitoring. Copper electrodes are often used to this aim since this metal presents interesting electrocatalytic properties towards nitrate reduction [2].

In this context, here we study possible improvements to the electrochemical analysis of nitrate by taking advantage of the detection capabilities of ensembles of copper nanowire electrodes (CuWNEEs).

CuWNEEs are prepared via template electrodeposition of copper within the nanopores of track-etched polycarbonate (PC) membranes. Three different preparation methods are compared which differ for the way used to contact the PC membrane with a flat disk Cu electrode used as supporting material. The best results in terms of sensor durability and reproducibility are achieved by pre-sputtering a thin gold film on the templating membrane and exploiting the adhesion property and ionic conductivity of a thin Nafion interlayer. The CuWNEEs are carefully characterized by electrochemical and SEM-EDS methods [3]. The voltammetric reduction of nitrate at CuWNEEs is characterized by a well-resolved cathodic peak at approximately -0.680 V vs Ag/AgCl. The detection limit by LSV is 1.7 μM and the dynamic range is 10-400 μM. Analytical results obtained with the CuWNEE sensor for nitrate analyses in mineral water samples compare satisfactorily with those achieved by standard chromatographic or spectroscopic methods.

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**SCANNING ELECTROCHEMICAL MICROSCOPY AND ANODIC STRIPPING VOLTAMMETRY TO CHARACTERISE SILVER NANOPARTICLES AT SOLID/SOLUTION INTERFACES**

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Because of their antiseptic properties, silver nanoparticles (AgNPs) are one of the most traded nanomaterials. These characteristics make them suitable as fillers in cosmetics, apparels, medical and food packaging.

The silver antiseptic properties are known since ancient times; however the mechanism of action of AgNPs is still debated. It seems that  $\text{Ag}^+$  ions released from metallic silver is the primary step for the bactericidal action. In fact, although AgNPs themselves can induce toxicity,  $\text{Ag}^+$  ions released from AgNPs surface appears to play a major role. For these reasons, recently, a variety of analytical methodologies has been developed for studying the mechanism of  $\text{Ag}^+$  release and quantify the amount released in various media such as acidic and hydroalcoholic mixtures [1]. To this purpose, electroanalytical techniques are very suitable, as they combine advantageous properties, such as sensitivity, speciation capability and low cost of the apparatuses.

In this paper, we present an investigation aimed at studying and monitoring the redox status of silver nanoparticles and the release of  $\text{Ag}^+$  at solid/solution interfaces of AgNPs-containing goods either on purposely synthesized or commercially available. This paper, in particular, highlights the stability of AgNPs embedded in various polymeric matrices, the amount  $\text{Ag}^+$  released when AgNPs are in contact with aqueous and organic media under different acidity conditions, and their concentration profiles established at the solid/solution interface.

The investigation is carried out by using scanning electrochemical microscopy (SECM) and voltammetry. SECM is a powerful technique, which allows electroanalytical measurements to be performed at interfaces with high spatial resolution. Voltammetry, especially in the stripping version, allows very sensitive and multielement analysis for the detection of metal ions at trace levels to be performed. Therefore their combination can represent a new and powerful analytical system to investigate on the quantity and fate of contaminants released from food packaging.

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## **ANALYTICAL CHARACTERIZATION OF ELECTRO-DECORATED ZnO NANORODS FOR GAS SENSING APPLICATIONS**

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Metal oxides (MO<sub>x</sub>) and noble metal modified MO<sub>x</sub> are a well-known sensing material for the detection of pollutants of automotive and environmental interest such as nitrogen oxides (NO<sub>x</sub>). [1-3] ZnO is considered a promising and versatile sensing material for solid-state semiconductor gas sensors because of the excellent sensitivity and selectivity figures of merit. In this contribution, nanostructured ZnO powders, synthesized by sol-gel method and properly desiccated, were electro-decorated by Au and Pd nanoparticles (NPs) using an in-situ process.[4] Metal NPs/MO<sub>x</sub> nanocomposites were then thermally annealed and subjected to a morphological and chemical characterization using transmission and scanning electron microscopies (TEM, SEM), as well as X-ray photon electron spectroscopy (XPS). Upon annealing, electro-decorated NP/ZnO powders were converted into ZnO nanorods whose surface was decorated by nanoscale gold or palladium retaining its spheroidal morphology. Surface chemical speciation of the catalytic nanophases was assessed by XPS and outlined the presence of elemental states even after the thermal treatment. The resulting nanocomposites could be finally used as active layers in chemiresistive gas sensors showing promising selectivity towards NO<sub>x</sub> species.

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**ORGANIC SOLVENTS AS GATE MEDIUM IN ELECTROLYTE-GATED THIN FILM TRANSISTORS**

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Electrolyte-gated thin film transistors (EG-TFTs) have attracted considerable attention in the field of organic electronics, owing to their capability of operating in liquid environment and at very low voltages. In this case, the transistor is gated through an electrolyte and the electrostatic coupling of the gate to the semiconductor channel is achieved through formation of electrical double layers (EDLs). The high capacitance of the EDL (few tens of  $\mu\text{F}/\text{cm}^2$ ) permits operating the device in the sub-voltage regime (below 1V). Solid electrolytes, ionic liquids, water and buffer solutions are most commonly employed as gating materials<sup>[1-3]</sup>. TFTs gated through organic solvents, mainly polar and water miscible solvents, have been also reported<sup>[4]</sup>. However, the mechanism of gating using organic solvents, such as alcohols and esters, is not completely understood. In the few works reported, the gating ability of organic solvents has been attributed to the presence of dissolved salt impurities.

In the present work, a thorough study on the use of different organic solvents as gate medium in TFTs is reported. In order to gain information on the operating mechanism, solvents of varying dipole moment and dielectric constant were tested. Both p- and n-type semiconductors were used, namely poly (3-hexylthiophene-2, 5-diyl) P3HT and zinc oxide (ZnO) respectively. In each case, the drain current was found to increase as the ratio of dipole moment with the dielectric constant ( $p/\epsilon$ ) decreased. Moreover, organic solvents solutions with varying ionic strength were also tested in order to examine if the formation of EDLs for organic solvents relies on the inevitable presence of salts traces dissolved in the organic liquids.

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**ELECTRODEPOSITION OF ALUMINIUM FROM IONIC LIQUIDS:  
CORROSION BEHAVIOR AND DEPOSITION PARAMETERS  
INFLUENCE**

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Since their discovery, ionic liquids (IL) have attracted a wide interest for their potential use as medium for many chemical processes, which vary from extraction, to catalysis, to organic synthesis.

In electrochemistry, their use as electrolytes has allowed electrodeposition of metal cations that were previously impossible to reduce in aqueous media. In particular, the first generation ILs (the so called chloroaluminated ILs) have made possible the deposition of Aluminium from his chloride salt. Despite the discovery of this process in the nineties, nowadays aluminium electrodeposition from Chloroaluminate ILs still maintains a number of open issues both on the side of fundamental science and technological aspects.

The present communication aims to shed some light on the aluminium electrodeposition process as concerns the effect of deposition parameters.

Thick Al-coatings (20  $\mu\text{m}$ ) were deposited on brass substrate at different temperature, potential and stirring conditions. Then, the coatings morphology and phase composition was investigated by means of optical and electronic microscope, rugosimetry and X-ray diffracton.

Finally electrochemical corrosion investigation was performed by means of Open Circuit potential recording, potentiodynamic polarization and electrochemical Impedance spectroscopy, to correlate Al-coating structure with their corrosion properties.

**IN-SITU STRUCTURAL CHARACTERIZATION OF SEMICONDUCTOR THIN FILMS FOR SOLAR CELLS SYNTHESIZED BY E-ALD**

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Scientific community is focusing attention on new compounds based on economic and low-environmental impact elements such as Cu, Sn, Fe and Zn. In particular, quaternary semiconducting materials based on the kesterite ( $\text{Cu}_2\text{ZnSnS}_4$ ) mineral structure are the most promising candidates to overtake the current generation of light-absorbing materials for thin-film solar cells. Electrodeposition is known as a low-cost semiconductor growth technique for applications in electronic devices. Surface limited electrodeposition of atomic layers, can be performed exploiting the Electrochemical Atomic Layer Deposition (E-ALD) technique to obtain sulphides thin films. In-situ SXR (Surface X Ray Diffraction) measurements were performed at ESRF (Grenoble) and focused on the investigation of the growth mechanism of Cu-S thin films. The growth of the film was monitored by following the evolution of some Bragg peaks after each E-ALD step. Results point to the occurrence of a self-standing film with a definite crystal structure after 15 E-ALD cycles. After the Bragg reflections are observed for the first time, only minor changes of the structural arrangement are registered.

Breadth and profile analyses of the Bragg peaks lead to a qualitative interpretation of the growth mechanism in the normal and in-plane directions, with respect to the Ag surface. Namely, the contribution of crystal strain and crystallite size were identified in the width of the Bragg reflections.

The preliminary interpretation of the experimental reciprocal lattice, coupled to the SEM investigation, suggests that the samples show a pseudo single crystal diffraction pattern. This can be described by a new hexagonal unit cell. The influence of the applied electric potential on the stability of the electro-deposited crystal structure was monitored by means of SXR measurements performed without applying any potential. A structural change was, in fact, registered, and correlated to the occurrence of the stable phases under conventional laboratory conditions.

**"INHERENTLY CHIRAL" ELECTRODES: TOOLS FOR CHIRAL VOLTAMMETRY**

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The development of artificial "intelligent" electrodes, capable to discriminate and quantify the enantiomers of chiral analytes is a quite attractive target in electroanalysis, and many approaches have been so far proposed, none of them however resolute.

An effective solution is now provided from a new class, which we have recently presented<sup>1-3</sup> and patented, of "inherently chiral" molecular semiconductors, whose stereogenic element is a tailored torsion in the electroactive conductive backbone. The coincidence of the element granting both electroactivity and chirality with the entire molecular backbone results in extraordinary chirality manifestations (such as circularly polarized luminescence), finely and reversibly tuned by the electric potential. Above all, enantiopure electrode surfaces can be easily prepared *e.g.* by fast electrooligomerization, mostly consisting of cyclic oligomers, highly electroactive and chiral, idealizing conducting polymers without ends and of high complexing ability; they are able to discriminate enantiomers of chiral molecules in terms of large peak potential differences (80-200 mV and more), with linear dynamic ranges for peak currents, thus affording enantiomeric ratio evaluation. The same spectacular enantioselectivity is obtained on chemically different surfaces of the same structural concept, which demonstrates the general validity of our proposed strategy. A simple reconditioning protocol affords performing more experiments on a single electrode. The new electrodes have been tested with very good results on chiral probes even very different and of applicative interest<sup>3</sup> (Dopa and methyl-Dopa, ofloxacin, norepinephrine, tyrosine, naproxen, catechines, ascorbic acid...), on different supports, including commercial screen printed ones, and in different media (aqueous and nonaqueous ones, as well as ionic liquid drops on screen printed electrodes).

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## SYNTHESIS AND CHARACTERIZATION OF “GREEN” METALLIC NANOPARTICLES FOR ELECTROCHEMICAL BIOSENSORS DEVELOPMENT

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New applications of nanoparticles (NPs) and nanomaterials are emerging rapidly. Green synthesis provides advantages compared to chemical and physical methods as it is cost effective, environmentally friendly, easily scaled up for large-scale synthesis without using high pressure, energy, temperature and toxic chemicals. One of the most considered methods is the production of metal NPs using biological systems such as microbes, fungi and several plant extracts [1].

In this work, we have synthesized metallic NPs using quercetin, a flavonol contained in some foods and drinks like red onion, black tea and red wine. First of all, we characterized the NPs using UV-Vis spectrophotometry to understand the right mechanism of the reaction, using different amounts of metal precursors and the same amount of quercetin [2]. Successively, the dimensions of the metal NPs have been determined by transmission electron microscopy (TEM) and dynamic light scattering (DLS) experiments [3]. At last, the electrochemical behavior of the metal NPs has been studied in the presence of different electrochemical mediators such as potassium hexacyanoferrate(III) ( $K_3Fe(CN)_6$ ) and ruthenium(III) hexamine chloride ( $Ru(NH_3)_6Cl_3$ ) and kinetic parameters such as the electrode electroactive area ( $A_{EA}$ ) and the electronic transfer rate constant ( $k_s$ ) were so determined [4]. The so characterized new NPs based electrodes, has been tested as bioanode and biocathode in a BFC based on cellobiose dehydrogenase and bilirubine oxidase, respectively.

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**CHARACTERIZATION OF ANODIC MATERIALS FOR LITHIUM-ION BATTERIES: THE CASE STUDY OF TiO<sub>2</sub>-RGO HYBRIDS FOR HIGH-POWER APPLICATIONS.**

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The market of Lithium-ion batteries (LIBs) is constantly increasing.[1] LIBs found applications into electronics and portable devices initially; however, actually they found even more uses in the automotive field, as they are replacing the NiMH technology especially considering hybrid and micro-hybrid electrical vehicles. [2] The electrochemical and chemical-physics characterization of the electroodic materials for LIBs is so a *new working field for the analytical chemists*. We report here the case study of the titanium dioxide/reduced graphene oxide (TiO<sub>2</sub>-rGO) composites used as anodic material in LIBs for high-power applications. TiO<sub>2</sub>-rGO hybrids were synthesized at different loadings of carbonaceous phase and used as anode materials in Lithium-ion cells, keeping in mind the feasibility of industrial scale-up. GO was synthesized from graphite [3], adsorbed onto commercial TiO<sub>2</sub> and reduced to rGO with chemical, photocatalytic and hydrothermal procedures. [4] TiO<sub>2</sub>-rGO obtained with the first two procedures showed good cycle stability, high capacity and impressive rate capability. The photocatalytic reduction was also applied on pre-formed electrodes reaching the goal of a further simplification of the anode production. The synthesized materials were in-depth characterized with a *multi-technique approach*, including *electrochemical methods*. The very promising performances, from the point of view of the specific capacity, were correlated with an effective reduction and with the maintenance of the 2D geometry of the final graphenic structure observed for the TiO<sub>2</sub>-rGO hybrids obtained by both the chemical and photocatalytic reduction procedure. The excellent electrochemical properties obtained at high C-rate (i.e. until 40C), the feasibility and the easy scalability of the production method show that these materials are promising candidate for their use as anode in LIB for power application.

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**SEQUESTERING ABILITY OF HYDROXYBENZOIC ACIDS TOWARDS ALUMINIUM(III) CATIONS: A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY**

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Aluminium is the most abundant metal of the Earth's crust; its compounds are frequently utilized as pharmaceutical drugs in human and veterinary medicine [1]. This metal is considered a highly neuro-toxic element due a common action in all living organism [2]. The toxicity of aluminium has led several researchers to seek new strategies in the treatment of aluminium intoxication. An emerging approach is represented by the aluminium chelation therapy, recommended for those patients who do not present any clinical improvement when exposure to aluminium is ended.

Phenolic acids are secondary plant metabolites widely diffused throughout the plant kingdom. Due to their ubiquitous presence in plant-based foods, a high intake of phenolic acids (25 mg – 1 g a day depending on diet) occurs [3]. The interest in these phenolic compounds lies on their known health benefits due to their antioxidant activity and ability as free radical scavengers. Vanillic acid, syringic acid and gallic acid belong to hydroxybenzoic compounds. Vanillic acid is one of the main degradation products of the wood constituent lignin [4]. Syringic acid exists in free form in plants and food, for example in wheat grain, in wheat-based food products [5] and in walnut husks. Gallic acid is found in many green plant tissues, especially in tea leaves, both in a free form and as a component of the polymers such as tannins and ellagitannins.

The purpose of this work was to study the complexation of vanillic acid, syringic acid and gallic acid with the Al(III) ion in the physiological conditions (*i.e.* in 0.16 M NaCl and at 37°C) by using a combination of experimental (potentiometric measurements, UV spectra and laser desorption mass spectrometry) and computational (density functional theory) tools in order to obtain the structural and electronic properties of the resulting complexes.

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## ANION INCAPSULATION BY $\text{Gd}^{3+}$ [15-METALLACROWN-5] COMPARTMENTS IN NEUTRAL AQUEOUS SOLUTION

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Encapsulation of guests in molecular containers has implications for chemical transformations, sensing, stimuli-responsive devices, separations and design of molecular materials. Molecular containers with open metal sites have drawn interest for their guest selectivity, catalytic activity and properties that arise from metal ions and concave cavities acting in a concerted mode. Metallacrowns (MC) are a unique class of self-assembled macrocycles with a metal-rich topology that resembles crown ethers.  $\text{Ln}^{3+}$ [15-MC<sub>Cu(II)</sub>-5] complexes have been developed into metallocavitands through the introduction of chiral  $\alpha$ -amino hydroxamic acid ligands bearing hydrophobic side chains, such as phenylalanine hydroxamic acid (pheHA).<sup>1</sup>

Dimeric compartments have been a consistent feature of  $\text{Ln}^{3+}$ [15-MC<sub>Cu(II)</sub>-5] complexes in the solid state; pheHA side chains of MCs associate through hydrophobic interactions generating a large dimeric compartment that encapsulates unsaturated dicarboxylate guests. Despite the great interest in synthesis and structural characterization of metallacrowns, a quantitative description of the host-guest complex formation in solution has not appeared yet and such supramolecular adducts have been mostly described in the solid state.<sup>2</sup>

Based on our experience on anion recognition and capsule self-assembling in solution,<sup>3</sup> here we report on the formation of dimeric compartments of  $\text{Gd}^{3+}$ [15-MC<sub>Cu(II)</sub>, S-pheHA-5] metallacrown with organic carboxylate guests with different features (size, saturation, shape) in neutral aqueous solution. The detailed nanocalorimetric analysis of the host-guest adducts provided key information on the species forming in solution, the stability of the compartments and the driving forces of the recognition process. Solution equilibria and speciation data allowed to address some of the issues related to compartment size and selectivity thus helping to establish a theoretical framework for predicting the structure of compartment inclusion complexes.

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## SEQUESTRATION OF DIFFERENT $M^{n+}$ CATIONS BY EDDS IN NATURAL FLUIDS

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Since ethylenediamine-N,N'-disuccinic acid (S,S-EDDS) is generally considered the biodegradable alternative to EDTA, its possible use for the sequestration of  $Ca^{2+}$ ,  $Sn^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Fe^{3+}$  is proposed in this contribution. For this purpose, new data on the binding ability of EDDS towards these cations have been obtained with potentiometric, voltammetric and calorimetric measurements at different ionic strengths and at  $t = 25^{\circ}C$ . Some important real multi-component fluids, namely fresh water ( $I \sim 0.003 \text{ mol dm}^{-3}$ ), urine ( $I \sim 0.40 \text{ mol dm}^{-3}$ ), sea water ( $I \sim 0.75 \text{ mol dm}^{-3}$ ), saliva ( $I \sim 0.11 \text{ mol dm}^{-3}$ ) and blood plasma ( $I \sim 0.21 \text{ mol dm}^{-3}$ ) were chosen as case studies for the evaluation of the sequestering ability of EDDS. The study of the speciation of EDDS in these media was performed drawing speciation diagrams in selected conditions, considering all the network of interaction between the "natural" components of the fluid and those studied in this work, EDDS and EDTA (at  $c_L = 1 \text{ mmol dm}^{-3}$ ) as sequestering agents and the metal cations,  $Ca^{2+}$ ,  $Sn^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ , and  $Fe^{3+}$  (generally,  $c_M = 10^{-5} \text{ mol dm}^{-3}$ ). This means that more than fifteen components and more than a hundred formation constants values are considered in each model. The comparison of the sequestering ability of EDDS and EDTA is done using objective tools, namely the pM (residual concentration of free metal cation), and pL<sub>0.5</sub> (total ligand concentration necessary to bind the 50% of metal in solution) [1]. In blood plasma, since the fundamental role of proteins cannot be modeled, the above mentioned parameters are useless, and the plasma mobilizing index (PMI) was adopted [2]. In general, it was found that EDDS is a good alternative to EDTA, which tends to bind  $Ca^{2+}$  and  $Mg^{2+}$  to an higher extent than EDDS. In particular, EDTA cannot be used as a sequestrant for  $Sn^{2+}$  when  $c_{Ca} > c_{EDTA}$ , and EDDS is more efficient than EDTA at  $pH < 8$ , particularly in urine, where carbonate is absent. On the contrary, in fresh water, where concentration of ions is very low, EDTA shows a greater ability in the sequestration of  $Sn^{2+}$  than EDDS. In sea water, the sequestering ability of EDDS and EDTA towards  $Fe^{3+}$  is comparable, although that of the former is slightly higher than that of the latter. In blood plasma, the PMI of EDDS towards  $Cu^{2+}$  is higher than that of EDTA.

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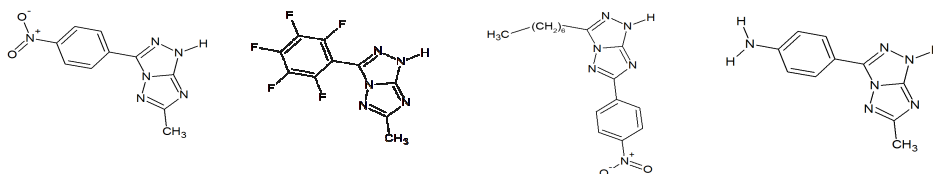
## THERMODYNAMIC STUDY ON TRIAZOLO-TRIAZOLE HETEROCYCLIC SYSTEMS

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Extensive replacement of carbon by nitrogen in aromatic heterocycles can be used not only for the tuning of electronic and structural features of the compounds but, depending on their structure, also for inducing totally new features such as N-H acidity and coordination ability to metal sites. Those features can be potentially relevant not only for biological applications, but also in the field of advanced materials [1,2]. Acid-base properties and complex formation with metal ions of four new triazolo[3,2-c]triazoles (Scheme) having substituents of different electronic character on the bicycle have been investigated at 25 °C in NaCl 0.5 M, as ionic medium, by using potentiometry, polarography and UV-Vis spectrometry (absorption and emission). The pH investigated spans between 0.5 and 12.



The study indicated that the neutral heterobicycle (HL) has acid-base properties strongly influenced by the presence of electron withdrawing or releasing groups at position 7 (it can deliver the H<sup>+</sup> to form the conjugated base L<sup>-</sup> and can accept up to two protons, forming the species H<sub>2</sub>L<sup>+</sup> and H<sub>3</sub>L<sup>++</sup>). By varying the groups attached at the heterocycle, a remarkable shift of pK<sub>a</sub> values, up to 5–6 units, is observed. The formation of the cationic species is accompanied by complex tautomeric switchings as shown by single crystal X-ray analysis and theoretical calculations [3,4]. The excited-state proton transfer also is influenced by the presence of electron withdrawing or releasing groups at position 7. Evidence of the formation of Me(II)-HL, mononuclear complexes, has also been obtained.

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**CHARACTERIZATION OF PHOTOTRANSFORMATION PRODUCTS OF AMINO-ACIDS.**

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The characterization of the phototransformation products of amino-acids in water bodies is part of an in-depth investigation of the formation mechanisms, the (photo)reactivity and the nature of dissolved organic matter (DOM) derived from the proteinaceous material. The irradiation of aromatic amino acids in aqueous solution produced compounds with similar spectroscopic properties of humic substances. The photochemical processes involving amino-acids could thus constitute an additional pathway for the bottom-up formation of humic substances in water bodies, which would be added to the network of reactions involving natural DOM [1]. In order to better understand the nature of these humic-like substances, in this work, the photodegradation products of L-tyrosine were characterized by UV-vis spectrophotometry, fluorescence EEMs, NMR, MS and pH-metric titrations. The MS results support the formation of a dimeric structure formed by a unit of L-tyrosine and a hydroxylated L-tyrosine, linked with an ether bond between the aromatic groups. The hydroxylation of the aromatic group was suggested also by NMR; the occurrence of the amino acid functions and the increase of the number of phenolic groups are confirmed by the chemical model proposed on the basis of pH-metric titrations data. The protonation constants and the concentrations of the protogenic sites of the L-tyrosine sub-products were estimated upon elaboration of alkalimetric titrations of the photodegraded L-tyrosine, using the BSTAC [2] software. A discrete model was used to interpret the experimental data. In order to fit satisfactorily the titration curves, a model with three protogenic sites was proposed and the same model can be used to explain the experimental data obtained with L-tyrosine irradiated for 16, 24 or 72 hours. The capacity of the L-tyrosine by-products to coordinate the copper cation was also estimated. The complexation capacity of the irradiated solutions seems to be a little higher compared to the parent amino-acid.

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**PRACTICAL APPLICATIONS OF THE SOLVOPHOBIC THEORY TO THE ANALYTICAL SEPARATION OF BIOMOLECULES BY REVERSED PHASE HPLC**

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Reversed phase high performance liquid chromatography (RP-HPLC) is widely applied to analyze a very broad range of molecules including charged and polar compounds. The separation mechanism, which is based on the interactions of the analytes with the hydrophobic chromatographic support in a polar mobile phase, has been deeply described by Csaba Horváth on the basis of the solvophobic force theory [1]. Accordingly, the distribution of a given analyte between the two phases depends on its polarity, the binding properties of the medium and the composition of the mobile phase, consisting of a hydro-organic mixture, which might contain a suitable buffer to control the protonic equilibrium. Decreasing the mobile phase polarity by adding more organic solvent reduces the hydrophobic interaction between the stationary phase and the analyte, resulting in weaker retention. The more hydrophobic the analyte the more time it will spend on the stationary phase and the higher the concentration of organic solvent that is required to promote elution.

This communication discusses the dependence of retention behaviour of a variety of biomolecules in RP-HPLC on the experimental parameters, such as flow rate, column length and ID, dwell volume, temperature, isocratic and gradient elution mode, variation of organic solvent concentration in gradient elution mode (gradient shape and duration). The influence of the considered parameters on the chromatographic behaviour of the selected compounds is discussed in the framework of the hydrophobic theory, both by changing one of the above parameters while keeping constant all the others. Also discussed is the use of DryLab modelling software, which allows the development of methods concordant with a Quality by Design (QbD) criteria, increasing flexibility in routine operations. The state-of-the-art will be illustrated with a few applications in the field of food and phytochemical analysis.

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**QUALITY BY DESIGN MEETS COMBINATION DRUGS:  
SIMULTANEOUS DETERMINATION OF CAPTOPRIL,  
HYDROCHLOROTHIAZIDE AND THEIR IMPURITIES BY  
CAPILLARY ELECTROPHORESIS**

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A fast and selective capillary electrophoresis method was set up for the simultaneous quantitation of captopril, hydrochlorothiazide and related impurities in the combined dosage form. The method was developed following Quality by Design principles, according to ICH guideline Q8 [1]. Captopril is characterized by the lack of a strong chromophore and by the presence of a proline-similar moiety which causes in solution the presence of cis-trans isomers that interconvert around the amide bond. A large part of the experiments of the scouting phase was dedicated to the selection among different pseudostationary phases based on micelles or microemulsions, with or without additives, in order to overcome detection and isomerization issues. The best results among the evaluated operative modes were obtained by cholate-based micellar electrokinetic chromatography with the addition of *n*-butanol and  $\gamma$ -cyclodextrin. Risk assessment tools were employed to define critical process parameters: temperature and voltage, concentration and pH of borate buffer, concentration of sodium cholate, *n*-butanol and  $\gamma$ -cyclodextrin. A symmetric screening matrix was applied to investigate the effect of the change of level of the selected factors on critical quality attributes, represented by critical resolution values and analysis time. Response surface methodology and Monte-Carlo simulation led to identify the design space, defined as the multidimensional region where any combination of the variables has been demonstrated to provide assurance of quality of the analytical performances. The application of the selected working point settings allowed the baseline separation of analytes to be obtained in less than 3 minutes. The method was validated and finally applied to a real sample of tablets.

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**POLYCYCLIC AROMATIC HYDROCARBONS DETERMINATION IN WATER: A COMPARISON BETWEEN “DRAW-EJECT” AND “EXTRACT-DISCARD” METHODS USING MICROEXTRACTION BY PACKED SORBENT COUPLED WITH GASCHROMATOGRAPHY – MASS SPECTROMETRY.**

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In this work, two different extraction procedures for the analysis of different polycyclic aromatic hydro-carbons (PAHs) in water by microextraction by packed sorbent (MEPS) have been compared in terms of sensitivity, reliability and time of analysis. The first method, called “draw-eject”, consists of cycle sequences of aspirations and injections in the same vial; the second one, called “extract-discard”, consists of a similar cycle sequence, but in this case the aspired sample is discarded into waste. The relevant partition equilibriums and extraction rates have been calculated by multivariate regression from the data obtained after MEPS gas chromatography–mass spectrometry (MEPS-GC–MS) analysis of 16 PAHs from water samples. Partitioning parameters for a priori prediction of solute sorption equilibrium, recoveries and preconcentration effects in aqueous and solvent systems have been calculated and compared for the two extraction procedures. Finally, real samples from sea, agricultural irrigation wells, streams and tap water have been analyzed. Detection ( $S/N \geq 3$ ) and quantification ( $S/N \geq 10$ ) limits were calculated for the extraction processes. Under the experimental conditions used for the “draw-eject” procedure, these values were in the range 0.5–2 ng L<sup>-1</sup> and 1.6–6.2 ng L<sup>-1</sup>, while for the “extract-discard” procedure they ranged from 0.2 to 0.8 ng L<sup>-1</sup> and from 0.8 to 2.0 ng L<sup>-1</sup>, respectively.

**QUALITATIVE AND SEMI-QUANTITATIVE ANALYSIS OF PHOSPHOLIPIDS IN RAT LIVER MITOCHONDRIA SAMPLES BY HPLC-IT/TOF-MS**

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Mitochondria are often referred to as the powerhouses of the cells. They generate the energy that our cells need to do their jobs. They have a complex structure containing two membranes, the outer and the inner one. Changes in any or all aspects of the mitochondrial lipidome will likely change the overall bioenergetics efficiency of mitochondria. For these reasons is important to characterize qualitatively and quantitatively the lipid species of mitochondria in different physiological and pathological conditions. Recently Bird et al. developed a high resolution LC-MS method to monitor major lipid classes in biospecimens. The method was applied to the analysis of liver mitochondrial lipids [1]. Aim of this work was to develop a method for the separation of lipid classes for both qualitative and semi-quantitative analysis of individual lipids isolated from rat liver mitochondria. Lipids classes were separated employing a HILIC column and data were acquired using high resolution full scan MS and MS/MS fragmentation spectra acquisition using LC coupled to IT/TOF-MS detector. Identification of phospholipid (PL) classes was first achieved by comparison of retention of standard compounds. Identification of molecular species was performed by using different integrated data: positive and negative high resolution mass spectra, negative MS/MS ion fragmentation spectra, LIPID MAPS database and literature data. Relative abundances (% values) were based on the ratio between the extracted ion peak area of each compound and the sum of areas of all detected compounds of the same class. Different glycerophospholipids and sphingolipids classes were detected, being phosphocholine (PC) and phosphoethanolamine (PE) the most represented ones.

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**GRAPHENE-MODIFIED SILICA SORBENT FOR SOLID-PHASE EXTRACTION OF BENZOTRIAZOLES AND BENZOTHIAZOLES FROM WATER**

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Graphene (GN) is attracting great interest in analytical chemistry, especially as novel sorbent for pre-concentration of a variety of compounds [1,2]. Its peculiar properties, i.e. large specific surface area, nanosheet morphology,  $\pi$ -electron-rich structure, and fast adsorption-elution processes make GN an excellent candidate to prepare high-performance materials for solid-phase extraction (SPE) applications [1,3]. In this work, a novel GN-based SPE procedure was developed for determination of benzotriazoles (BTRs) and benzothiazoles (BTs) in water samples. BTRs and BTs are among the ubiquitous emerging pollutants not completely abated by wastewater treatment [4]. As a result they can be found in environmental waters at concentrations from about 1 to 100  $\mu\text{g L}^{-1}$  [5]. In this work, silica microparticles were derivatized with monolayer GN flakes and tested as fixed-bed sorbent (200 mg) for pre-concentrating BTRs and BTs, prior HPLC-UV analysis. Trueness and precision were evaluated on tap water samples spiked in the range 1-1000  $\mu\text{g L}^{-1}$ . Elution with methanol (10% v/v acetic acid) gave average absolute recoveries in the range 70-86% (RSDs<15%,  $n=4$ ). Sample volumes up to 500 mL and evaporation of the SPE extract by nitrogen gas provided enrichment factors up to 1000. The GN-modified silica preserved its adsorption efficiency for at least 10 extractions. The optimized procedure was then assessed on raw river water, followed by HPLC-MS analysis. Experiments are ongoing to evaluate accuracy, linearity and sensitivity.

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**OVERCOATED SOLID PHASE MICROEXTRACTION FIBER: A NEW APPROACH FOR DIRECT ANALYSIS IN RAW URINE SAMPLES**

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Solid phase microextraction (SPME) is a fast and user friendly sample preparation technique able to perform analytes extraction and pre-concentration at the same stage. Sampling of low volatility analytes in aqueous samples by SPME is carried out by direct immersion of the fiber. However, this procedure may have some drawbacks when complex matrices are analyzed because the coating can be irreversibly damaged by the adsorption of the matrix macromolecules. Recent studies point out the great endurance of polydimethylsiloxane (PDMS) coating leading to the development of a brand new concept of fibers i.e. the overcoated fibers [1,2]. The characteristic of these fibers is the modification of existing commercial SPME fiber coatings with a thin layer of PDMS. Overcoated fibers have shown very promising results in complex food matrices such as the whole grape and strawberries pulp without any further sample pretreatment [2]. Bio-clinical applications of these new laboratory-made fibers are not yet explored. Clinical analyst often have to deal with complex matrices. As consequence, the application of overcoated fibers in clinical investigations can determine a significant enhancement because SPME analysis can be carried out directly in complex biological fluids reducing or even avoiding the dilution step generally performed [3]. In this work, polycyclic aromatic hydrocarbons (PAHs) were taken into account in a comprehensive evaluation of the PDMS/DVB/PDMS fiber in raw human urine. A survey on the thermodynamics and kinetics of the extraction process was performed along with the investigation of the fiber endurance. Later on, the overcoated fiber was used in direct immersion mode to develop a fast and easy protocol for the analysis of urinary PAHs by SPME-GC-MS/MS. The proposed protocol was finally evaluate on a real case scenario analyzing urine samples of smoking and non-smoking volunteers.

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**ORGANIC BIOELECTRONICS: A PROMISING CHOICE FOR THE DEVELOPMENT OF THE NEXT GENERATION OF POC DEVICES**

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Point-of-care (POC) biosensors are integrated diagnostic systems employed for the detection of clinically relevant analytes in biological fluids such as blood, urine and saliva. These devices offer the advantage to provide rapid results directly where the information is needed (*e.g.* patient’s home, doctor’s office or emergency room), thus facilitating an earlier diagnosis and a prompt patient’s treatment. Various technologies have been proposed for the realization of POC biosensors including label-free techniques based on optical, mechanical and electrochemical transducers. However, reliable, quantitative and ultrasensitive devices have been not yet commercialized. Electronic biosensors based on organic field-effect transistors (OFETs) are a promising choice for the development of the next generation of POC devices [1]. These biosensors can be combined with integrated electrical circuits, microfluidic systems and wireless technologies. Furthermore, they offer high sensitivity, biocompatibility and possibility to produce all-printed low-cost biosensors in flexible and disposable formats. Among them, electrolyte-gated (EG)-OFETs have been identified as ideal candidates for biosensors development as they operate at low voltages directly in aqueous buffer solutions. Two EGOFET architectures useful for realization of POC devices will be presented. In the first, the biological recognition elements are anchored on the organic semiconductor surface [2], while in the second the biomolecules are confined on the gate electrode [3]. Using these configurations ultrasensitive label-free immunosensors for the detection of C-reactive protein (CRP), a specific biomarker of inflammatory and infection diseases, have been developed. The specific features of the proposed EGOFET biosensors as well as their analytical performances will be discussed.

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**SMARTPHONE-INTERFACED 3D PRINTED BIOSENSORS INTEGRATING BIOLUMINESCENT “SENTINEL CELL” FOR TOXICITY TESTING**

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Global security threats have become a major concern and their early detection represents a major challenge to current monitoring technologies. The routine monitoring of water, food and the environment for chemical and biological threat agents is often hampered by the fact that available techniques usually require clean samples and sophisticated equipment, and are thus unsuitable for real-time, cost-effective and on-field routine monitoring. We previously demonstrated the feasibility of implementing enzyme-based assays with bio-chemiluminescence detection into smartphones using cartridges and adaptors fabricated with user-friendly, low-cost 3D printing technology [1,2].

Here we report a portable toxicity sensor incorporating bioluminescent (BL) whole-cell biosensors into a smartphone-based device. We fabricated a 3D printed smartphone adaptor and ready-to-use cartridges integrating an array of bioluminescent cells. We demonstrated the feasibility to accurately detect and quantify the BL signals of genetically engineered human cell lines expressing different luciferases and exploited them as a toxicity sensors using a smartphone. An android app was also developed to provide a user-friendly built-it data analysis. A limit of detection of 5000 Hek293T cells expressing the green-emitting luciferase, was obtained and toxicity test showed performance comparable to those obtained using portable cooled CCD camera, confirming the suitability of this approach. Conscious that huge efforts will be required to extend the lifespan of the integrated cells without affecting the analytical performance of the system, we believe that it could find significant application as rapid alerting tool, suitable for detecting the presence of harmful pollutants in civil and military water supplies, for terrorism surveillance, and for detection of health threats in drinking water in developing countries.

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**LABEL AND LABEL-FREE ELECTROCHEMICAL BIOSENSING PLATFORMS FOR microRNA DETECTION**

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microRNAs (miRNAs) are considered powerful diagnostic and prognostic clinical biomarker candidates for many human diseases. These include a broad range of cancers, heart diseases, immunological and neurological diseases. In particular, regarding cancer, miRNA profiles not only distinguish between normal and cancerous tissues and identify tissues of origin, but they can also discriminate between different subtypes of a particular cancer. Recently, the awareness of the presence of miRNAs not only within cells but also in body fluids, paves the way for noninvasive biomarker analysis. Furthermore, since deregulated miRNA expression is an early event in patients with cancer, measuring circulating miRNA levels, may also be useful for early diagnosis, obtaining high advantages to the success of the treatment.

Actually, there are several techniques for the detection of miRNAs each of them with their own unique advantages and disadvantages. However, most of these approaches are not compatible with Point-Of-Care Testing. A great deal of effort has been devoted to develop new compact analytical methods for miRNA decentralized analyses that possess appropriate sensitivity without PCR. Thus, electrochemical genosensors have emerged as particularly attractive options for miRNA detection in terms of simplicity of use, assay time and amount of sample required.

In this paper, we report the development of a genosensor based on faradaic impedance spectroscopy coupled to an enzymatic amplification of the hybridization event. Biotin labeled liposomes, have been also tested as a functional tether for the enzyme molecules.

Moreover, in a further approach, a label-free impedimetric genosensor for miRNA detection, using a miniaturized, polymer-modified sensor has been developed. In particular, a polymer bearing an intact biotin moiety available for streptavidin binding has been used. This fact gave rise to the ability to nanostructure the sensor surface increasing the capture probe immobilization efficiency in terms of orientation, loading and steric hydrance.

Both the label-free and label-based approaches allow the detection of miRNAs in cancer cells and the results are, herein, reported.



**BIOSENSORS FOR PESTICIDES DETECTION: AN INNOVATIVE ELECTROCHEMICAL DNA-BASED SENSOR FOR ACETAMIPRID**

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DNA-based biosensors have recently been reported as a promising alternative to traditional methods for pesticide analysis and, in general, for environmental monitoring, having the capacity to combine a low cost for the realization of the artificial receptors with an efficient analytical performance. Recently, a DNA aptamer specific for acetamiprid, a diffused neonicotinoid insecticide has been described, giving the possibility to develop new kinds of analytical tools. In this work, an innovative electrochemical DNA aptasensor for acetamiprid is presented. The DNA-based sensor is based on a competitive binding assay between the analyte and a complementary DNA sequence. Firstly, polyaniline film and gold nanoparticles were progressively grown on a graphite screen-printed electrode surface via electro-polymerization and electrochemical deposition, respectively. The polyaniline-gold modified surfaces were then modified with a mixed monolayer of the thiol-tethered DNA aptamer and a spacer thiol. The DNA-based sensor realized with a solution containing a fixed amount of biotinylated complementary sequence and a variable amount of acetamiprid was incubated. An enzyme-amplified detection scheme, based on the coupling of a streptavidin-alkaline phosphatase conjugate and biotinylated secondary aptamer has been applied. The enzyme catalyzed the hydrolysis of the electroinactive 1-naphthyl-phosphate to 1-naphthol. This electroactive product was detected by means of differential pulse voltammetry. As the concentration of acetamiprid is increased, less complementary sequence can bind to the aptamer and the measured response decreases. Thus, the lower the signal, the more analyte is contained in the sample. After various experimental parameters optimization, a calibration curve between 0-1000 nM acetamiprid concentration range was obtained.

**ULTRASENSITIVE DETECTION OF MULTIPLE GENETIC LEUKEMIA BIOMARKERS BY MEANS OF SURFACE ENHANCED RAMAN SPECTROSCOPY**

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In the field of cancer research there is an increasing need for highly sensitive, accurate and reproducible technologies which would allow the detection of very low concentrations of biomarkers associated to the onset of a disease and the responsiveness to therapy. Surface-Enhanced Raman Spectroscopy (SERS) is emerging as a very promising tool for its higher sensitivity, specificity [1] and better multiplexing capability compared to the conventional analytical methods.

Here, we present a new sensor based on the use of SERS on a specifically designed 2D solid substrate, in order to improve the stability of the system and to obtain a regularly distributed array of hot spots. For this purpose, a nanostructured surface made of polymeric pillars embedded in a gold layer is tested in a biochemical assay for the simultaneous detection of multiple genetic leukemia biomarkers. The sensor is built as a sandwich assay between the surface, functionalized with thiol-modified oligonucleotides, and gold nanoparticles, labeled with different Raman reporters. Thanks to the combination of the favorable properties of our SERS substrate and the use of nanoparticles, we were able to detect simultaneously a leukemia biomarker (WT1 gene [2]) and an housekeeping gene with low picomolar sensitivity [3].

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**AFFINITY SENSOR FOR 2-FURFURAL BASED ON SYNTHETIC RECOGNITION ELEMENTS AND ELECTROCHEMICAL TRANSDUCTION AT SCREEN PRINTED CELL**

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2-Furfural (2-F) and other furanic derivatives are natural occurring substances deriving from the dehydration of five carbon sugars as xylose and arabinose, and from the reaction of reducing sugars with amino acids, particularly at high temperature. They are present in many foodstuffs, as milk, infant formula, honey, fruit juices, oils, wines, where they can also be considered as potential indicator of bad storage conditions. Moreover 2-F is very important as a precursor of furan based biofuels. Usually the analysis of furanic derivatives is successfully performed by chromatographic procedures, but methods for rapid, out of the lab determination are more and more required. Bio and chemo sensors are particularly suited for determinations of this kind.

Here a chemosensor for 2-F is proposed, based on a synthetic recognition element with higher chemical and thermal stability than natural receptors, and which can be reused multiple times.

The receptor is a molecularly imprinted polymer based on methacrylic acid as functional monomer, and divinylbenzene as cross-linker. The polymer is synthesized as a layer (10-30  $\mu\text{m}$  thick) directly over a screen printed cell with graphite working electrode as previously reported [1]. The reduction of 2-F at this electrode takes place at around -1.4 V (vs Ag reference electrode), sufficiently higher than the onset potential of the solvent (water) to allow a reproducible detection of the peak for analytical purposes.

SWV has been used for quantification, since it is the most sensitive method. The conditions were optimized by experimental design.

The peak current increases with 2-F concentration in the range about  $10^{-7}$ - $10^{-3}$  M, with a lower detection limit of about  $10^{-7}$  M. The dose-response curve is linear in the whole concentration range in the logarithmical form of the variables, so that this relationship is suggested for quantification. The sensor has been proved to be selective for 2-F even in complex matrices, as wine or extract of olive oil.

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**PLATINUM NANOSPHERES AND NANOFLOWERS MODIFIED ELECTRODES FOR DIRECT ELECTRON TRANSFER OF LACCASE FROM *TRAMETES VERSICOLOR***

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In recent years, a great deal of research has focused on the development of new methods for the preparation of nanosized transition metal; in particular, extensive studies on nanostructured materials have been carried out toward finding new electrodic materials able to enhance the direct electron transfer (DET) of redox proteins. Pt is a very common electrode material due to its ability to facilitate electrochemical reactions; the development of novel and simple methods to obtain Pt nanomaterials have attracted particular interest due to their high performance in electrochemical sensors.

In this research, Pt nanostructures were realized by an innovative and simple one-step template-free electrodeposition on Pt electrodes [1] obtaining different nanostructured electrodic materials characterized by Pt nanospheres and Pt nanoflowers differing in shape and size by changing deposition parameters. The characterization of the realized structures by scanning electron microscopy confirms the homogeneous distribution and nanoscaled size of Pt nanospheres and Pt nanoflowers. The obtained new Pt nanostructures were used as electrodic material to promote the DET of Laccase, a multicopper oxidase.

Laccase from *Trametes versicolor* was immobilized onto different Pt nanostructures with Nafion membrane as physical entrapping agent. Direct electrochemistry of laccase on Pt nanostructures was achieved with high efficiency due to the physicochemical characteristics of the new Pt nanomaterials. The enhancement of direct electron transfer can be attributed to the nanostructured modification induced onto the electrode surface.

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**ALL-IN-PAPER ELECTROCHEMICAL SENSOR TO DETECT PHOSPHATES**

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Nowadays, demand for sensitive, rapid and cost-effective sensors suitable for environmental monitoring, clinical diagnosis, food safety, is rapidly increasing. Electroanalytical techniques, thanks to their simplicity, rapidity, cost effectiveness, inexpensive instrumentation, low maintenance, portability, are being established as the easiest methods to develop sensors for the preliminary screening analyses, avoiding to consume time and money in laboratories equipped with expensive and/or big instrumentation, e.g. ICP-MS, AAS, HPLC, GC. Particularly, screen-printing technology emerges as the most useful tool to develop this kind of platforms because of its well known properties.

Coupled to this capability, paper is rising as an effective substrate to build up sensor (colorimetric paper-based sensor have been largely reported); during last decade, many works have been reported on the production of paper-based electrochemical sensor [1].

Herein we report a novel approach to develop electrochemical sensor exploiting the great properties of paper, beyond its reduced cost, by coupling screen- and wax-printing technology. Paper is firstly modified with reagents by an easy drop casting procedure and then, sensor with three-electrode configuration is printed on it. This simple strategy allows to fabricate a platform which contains all the reagents required for a reaction and to detect analyte in a reagentless mode. We demonstrate the suitability of this strategy towards the detection of phosphate ions *via* formation of phosphomolybdate complex, by screen-printing carbon black-modified ink onto filter paper containing an acidic solution of molybdate ions, and performing cyclic voltammetry measurements reaching a limit of detection at micromolar level and a satisfactory repeatability (RSD < 5%) of the developed platform.

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**DEVELOPMENT AND COMPARISON OF ELIME ASSAY AND REAL-TIME PCR FOR DETECTING OF SALMONELLA IN IRRIGATION WATERS**

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In the last years, fresh and ready to eat vegetables, contaminated with *S. Napoli* and *S. Thompson*, from Campania areas have been the cause of repeated food alerts in the EC. Contaminated waters used to irrigate crops have been demonstrated to represent the main risk factor. To protect consumer health and safety the food business, operators have to ensure the absence of this pathogen in a defined water volume. Since the standard culture method for detecting *Salmonella* (EN/ISO 6579) requires up to 5 days to produce results, the need to develop rapid methods represents an important issue for the authorities and producers. The aim of the present study is the development of two different techniques to evaluate the *Salmonella* presence in irrigation waters: an ELIME assay and a Real-time PCR. In particular the ELIME assay is based on the use of magnetic beads (MBs), as support of the immunological chain, coupled with a strip of 8-magnetized SPEs. The product of the enzymatic reaction is quickly measured by chronoamperometry. The system was optimized by testing different kinds of MBs, blocking agents, monoclonal antibodies and merging the two conventional steps of incubation in a single step. In the optimized conditions, the LODs were found to be  $10^4$  and  $10^5$  CFU/ml for *S. Napoli* and *S. Thompson*, respectively.

The Real-time PCR employs primers and a specific LNA fluorescent probe able to amplify a region of the *trRSBCA* gene, conserved in all *Salmonella* serotypes, and an internal amplification control to check false negative results. The LOD was calculated to be 10 CFU/mL.

After that, inclusivity and exclusivity tests were carried out demonstrating the ability of both methods to detect selectively different salmonella serovars, most commonly isolated from environmental sources. Finally the two systems were applied to experimentally inoculated irrigation water samples pre-enriched in two different broths. Results showed that the minimum pre-enrichment time, necessary to reveal *Salmonella*, was 6 and 10 hours for Real-Time PCR and ELIME assay, respectively.

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## DESIGN, FABRICATION AND CHARACTERIZATION OF ULTRA-SENSITIVE FLOW-THROUGH OPTOFLUIDIC MICRORESONATOR FOR (BIO)SENSING APPLICATIONS

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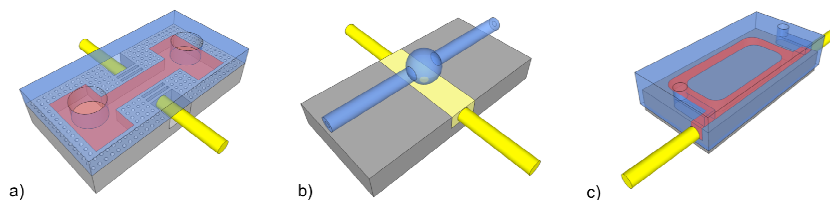
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This work describes the design, fabrication and characterization of three optofluidic microresonators, namely a photonic crystal resonator, a bubble resonator, and a ring resonator, and reports preliminary results on their use in flow-through optofluidic sensing applications. The microresonators, based on different operation principles, are fabricated by using different technologies and functionalization strategies, based on biological and synthetic polymeric receptors. The final objective is the exploitation of such ultra-sensitive optofluidic resonant (bio)sensors for the optical detection of neopterin, a sepsis biomarker, with high sensitivity and low detection limit, thus breaking a new ground in the biosensors and lab-on-chip arena and healthcare and point-of-care applications. Neopterin is selected as target analyte being the discrimination of viral and bacterial sepsis in intensive care patients or the fast identification of the origin of infection a key issue in this field. Moreover, the growing request of physicians for point-of-care devices capable of performing fast and reliable analysis at patient-level, thus enabling a quick and effective diagnosis and therapy, as opposed to laboratory-level, further supports the final goal of the present work.



**Figure 1** – Schematic representation of a) photonic crystal resonator, b) bubble resonator, c) ring resonator.

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**PEPTIDE BASED SENSING SYSTEMS FOR THE SELECTIVE DETECTION OF CHLOROGENIC ACID DERIVATIVES**

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The aim of this work was the evaluation of the binding capacity of a synthetic peptide, designed by a computational approach, towards a series of phenolic compounds involved in food chemistry. The peptide was designed allowing two possible anchoring site for chemical binding to sensor surface: a glycine residue that can be coupled to carboxylic groups and a cysteine for direct immobilization on metals surface such as gold electrodes. The peptide affinity towards chlorogenic acid, used as model target molecule, was performed following the fluorimetric quenching of a tryptophan of the peptide sequence upon binding with the target molecule. In order to apply this peptide to the development of an electrochemical sensors for the selective determination of phenolic compounds in food, we carried out a screening of possible interfering analytes using cyclic voltammetry and differential pulse voltammetry as detection strategy. To avoid electrode fouling disposable screen printed electrodes were used for electrochemical detection. The study was carried out in buffered solution at pH 7.0 without the addition of organic solvents. Moreover the immobilization of the cyclic peptide was performed also on gold nanoparticles (AuNPs) using two different approaches. The former followed the immobilization of the peptide via S-S group on pre-formed AuNPs, whereas the latter approach was designed with the aim to bind the cyclic peptide during AuNPs formation in reducing medium. Data on the application of the different material both to optical and electrochemical detection of chlorogenic acid, caffeic acid, coumaric acid and ferulic acid will be presented.



**STUDY OF PHOTOCHEMICAL TRANSFORMATION OF TWO SUNSCREENS IN SURFACE WATERS BY HRMS**

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The organic UV filters are frequently added to personal care products such as cosmetics, skin creams, body lotions, shampoos, spray and hair dyes in order to prevent damage caused by ultraviolet light. For their hydrophobicity, leading to accumulation in biota or sediments, and their potential action as endocrine disruptors, the environmental fate of these organic substances is becoming of increasing concern.

In the present study we focused on two organic UV filters, ethylhexyl methoxy cinnamate (EHMC) and 2-ethylhexyl-4-(dimethylamino)benzoate (OD-PABA).

Although EHMC is one the most used UVB filters worldwide and it is well tolerated by the skin, it has some side effects including its ability to produce reactive oxygen species and estrogenic properties both *in vitro* and *in vivo*.

OD-PABA was also among the first compounds to be used as sunscreens, but from 2008 it is gradually being replaced by other organic UV filters because of the increasing evidence of photo-allergic reactions.

To assess their environmental persistence and photoinduced transformation, the sunscreens were subjected to direct photolysis, by exposure to UVA and UVB radiation, whereas the environmental degradation upon indirect photochemistry was also simulated by the use of heterogeneous photocatalysis with titanium dioxide. The formation and evolution of transformation products (TPs) was followed via HPLC-HRMS for both processes. The study of MS<sup>n</sup> spectra, obtained using a LTQ Orbitrap mass spectrometer with ESI ion source, provided useful information to identify the TPs formed through the degradation.

For EHMC, the main TPs detected in the direct photolysis process were the 4-methoxybenzaldehyde, plus a hydroxylated derivative and two dimeric species. Through the use of heterogeneous photocatalysis, seven addition TPs were identified, most of them resulting from the further degradation of TPs formed through direct photolysis and that might be also found in aquatic systems. For OD-PABA the direct photolysis is shown to play a key role in phototransformation and this fast process is expected to be the main attenuation route in sunlit surface waters. The main detected TPs of OD-PABA would involve a dealkylation or hydroxylation/oxidation process in both direct photolysis and indirect phototransformation.

## **BROMINATED FLAME RETARDANTS IN EDIBLE BIVALVES: FOOD CONTROL AND LACK OF SPECIFIC LEGISLATION**

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Polybrominated diphenyl ethers (PBDEs) are among the most important classes of additive brominated flame retardants (BFR). They have been identified in every compartment of aquatic ecosystems, from abiotic to biotic matrices, and in industrialized areas as well as in remote ones. PBDEs are persistent, highly bioaccumulative and can move up to high trophic levels through biomagnifications [1].

Due to the growing concern about the potential health risks of PBDEs, their characterization in biological organisms that are widely and frequently consumed as food is paramount. Furthermore, at present there is no local or international regulatory limit for PBDEs in food.

We investigated the spatial distribution and levels of PBDEs in two bivalve species (*Mytilus galloprovincialis* and *Ruditapes philippinarum*) sampled from the north-western coast of the Adriatic Sea, that are widely used in the regional cuisine. Analyses were carried out using analytical protocols already developed in the laboratory [2] and were performed by HRGC/HRMS for the simultaneous determination of 14 PBDE congeners in biota tissues. Quantifications were carried out by isotope dilution.

The total concentrations ranged from 0.003 ng g<sup>-1</sup> wet weight to 6.66 ng g<sup>-1</sup>, with strong variations within the same sampling site. No significant differences between species were found. As for decabrominated diphenyl ether, in literature the determination of the BDE-209 is often neglected. However, the results of this study show that Deca-BDE is one of the most abundant congeners. However high, the levels of PBDEs in the samples collected near an industrial area subject to a fishing ban are lower than the values of four edible samples gathered in aquaculture farms and intended for human consumption. The concentrations of ΣPBDEs detected in this study are relatively higher than those reported for the Mediterranean area.

Considering the potentially toxic effects of PBDEs and the lack of specific legislation, this study emphasizes the need to further investigate these compounds and to establish maximum levels in foodstuff.

This work was funded by the Italian Ministry of Education, Universities and Research (MIUR) through the project PRIN (Prot. 2010AXENJ8).

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**A NEW CLASS OF MALDI MATRICES FOR HARDLY IONIZABLE COMPOUNDS BASED ON SUPERBASIC ALKYL-SUBSTITUTED BISPHOSHAZENE PROTON SPONGES**

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To date, MALDI-MS is largely employed for the characterization of high molecular weight biomolecules in genomics, proteomics and tissues imaging [1]. The use of MALDI in detecting low molecular weight (LMW) compounds in metabolomics, including lipidomics, remains challenging especially due to the spectral background produced by conventional organic matrices below  $m/z$  800. Beside the molecular weight, another key issue to be considered is the chemical nature of the analyte; for instance, free sterols and oligosaccharides are considered poor candidates for MALDI-MS due to their very low ionization yield [2]. Chemical derivatization such as conversion into picolinyl esters or sulfates for sterols and 1-phenyl-3-methyl-5-pyrazolone for saccharides are usually employed [3]. Spectral interferences in the low  $m/z$  range can be overcome [4] by several approaches including the use of an ionless matrix such as the Alder's proton sponge 1,8-bis(dimethylamino)naphthalene (DMAN). However, DMAN is still ineffective for the deprotonation of unconjugated hydroxyl moiety (-OH) of alcohols or saccharides. Very recently, superbasic proton sponges based on the 1,8-bisphosphazenylnaphthalene (PN) proton pincer motif and diverse P-alkyl substituents have been synthesized, via a Kirsanov condensation, using 1,8-diaminonaphthalene [5].

In this communication, the potential of such compounds as MALDI matrices has been demonstrated for the first time by analyzing intact (i.e. underivatized) sterols and oligosaccharides. The effectiveness of this new class of matrices in lipidomic studies is also demonstrated by the simultaneous determination of cholesterol, free fatty acids, lysophospholipids and phospholipids in egg and brain samples.

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**HRMS ANALYSIS OF ORGANIC FRACTION IN PM<sub>2.5</sub>: POST-RUN DATA ANALYSIS WORK FLOW AND THE ROLE OF IONIZATION SOURCE.**

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To study the formation and transformation processes of airborne particulate, an accurate and representative characterization of the organic composition is pivotal. For a comprehensive characterisation of organic matter graphical visualization methods of molecular formula parameters are often applied to deal with the large data sets. High Resolution Mass Spectrometry (HR-MS) based on Orbitrap technology has been shown to be a powerful tool to determine the exact mass and molecular formulas of the compounds present in the organic fraction. This technology can resolve thousands of  $m/z$  signals belonging to thousands of compounds present in the organic fraction of secondary atmospheric aerosols. A key step in obtaining reliable molecular formula from HR-MS mass spectra is a post run data work flow to associate the most probable molecular formula to each signal.

In this contribution we will present a fully automated algorithm for filtering the molecular formula candidates obtained by HR-MS and to select the chemically most likely ones and avoid the presence of false positives. The algorithm involves first a physical blank subtraction step followed by molecular formula filtering based on heuristic rules: (1) restrictions for the number of elements; (2) LEWIS rules; (3) hydrogen/carbon ratios, (4) element ratio of nitrogen, oxygen, and sulphur versus carbon; (5) isotopic patterns; (6) mass errors.

The developed algorithm has been applied to study the effect of different ionization sources and polarity to characterise the organic fraction in winter and summer PM 2.5 samples collected in Padua. NanoESI (nano electrospray) and APPI (atmospheric pressure photo-ionisation) sources were used in direct infusion to analyse the aerosol samples in the  $m/z$  range 100-900 to identify sensitivity and characteristics of the two ionisation techniques. Kendrick Mass Defect and Van Krevelen methodology were used to identify mass distributions and compound classes present in the mass spectra.

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**IDENTIFICATION OF ISOBARIC PHOSPHOLIPIDS IN SEAFOOD: THE KEY ROLE OF HIGH RESOLUTION MASS SPECTROMETRY**

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In the last decade, the increasing awareness of the benefits that the lipid fraction of seafood may have for human health [1] has led to a growing interest towards the molecular characterization of seafood lipids and of their hydrolytic or oxidative by-products. Mass spectrometry-based lipidomics approaches, such as shotgun MS [2] or LC-MS [3], have proved to be very useful to fulfill this goal.

As part of a comprehensive investigation concerning the effects of storage-induced lipid hydrolysis on seafood quality and safety, the combination of high efficiency hydrophobic interaction liquid chromatography and high resolution mass spectrometry (HILIC-HR-MS) has been recently tested in our laboratories. The method has been applied to a systematic identification of the *lyso* forms of the major class of phospholipids in fish muscles, i.e., phosphatidylcholines (PCs). The high mass resolving power and accuracy of an Orbitrap MS analyzer has permitted to unveil a very complex scenario, that could not even be imagined using low resolution MS. Indeed, several couples of closely eluting and almost isobaric *lyso*-PCs (LPCs) species ( $m/z$  ratios differing on the third decimal place), have been detected in the lipid extracts of gilthead sea bream (*Sparus aurata*). The careful combination of high resolution MS and high (HCD) and low collisional energy (linear ion trap) MS/MS has led to identify them, respectively, as protonated or sodiated adducts of different LPCs [4]. As a result, 43 proton and 28 sodium adducts of LPC species have been identified. Applications of this approach will be discussed during the present communication to emphasize the key role played by high resolution mass spectrometry in lipidomics investigations.

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**ANALYTICAL STRATEGIES TOWARDS THE ASSESSMENT OF “GLUTEN-FREE” PRODUCT SAFETY: LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY *vs* IMMUNOSENSING**

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Celiac patients should feel confident in the safety of foods labelled or expected to be “gluten-free”, containing less than 20 mg gluten/kg [1]. As for food safety assessment, a growing area is the development of biosensors in response to high sensitivity, speed, portability and low cost [2]. Targeted proteomic approach based on mass spectrometry (MS) has likewise shown great potential for allergen analysis, overcoming some limitations associated to antibody-based methods, improving confidence in protein determination [3]. The present work deals with the development of two different analytical strategies, based on immunosensing and liquid chromatography-electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS), for conformity assessment of “gluten-free” declared foods. In particular, the immunosensor configuration involved an indirect competitive amperometric immunoassay based on gliadin-functionalized gold nanoparticles-modified carbon screen-printed electrodes. However, a great limitation of antibody-based assays, among which the most exploited enzyme-linked immunoassay (ELISA), is the cross-reactivity of anti-gliadin antibody towards prolamin fractions of other grains. Thus, potential of a multiplex shotgun MS-based proteomic method was investigated to detect individually celiotoxic cereals, i.e. wheat, oats, barley and rye, by monitoring unique marker peptides in a single chromatographic run. A comparison between the investigated strategies highlights their complementarity, responding to the needs for rapid screening, as addressed by the immunosensor assay, and prolamin-specificity of LC-ESI-MS/MS.

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**IDENTIFICATION OF ACTIVE SPECIES FROM A PLANT EXTRACT AGAINST CANCEROUS CELL PROLIFERATION: A MICRO LC-MS/MS STUDY**

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Nowadays, scientific research is focused on polyphenol biological properties, as they are so connected to the inhibition of free radical processes linked to many diseases. It is well known that high levels of polyphenols play a preventive and protective role against several type of cancer as well as the reduction of coronary artery disease. In particular, anthocyanidins are known to catch free radicals after the donation of hydrogens present in the hydroxylic groups, acting in this way as antitumoural [1].

Last year the aqueous extract of an oriental plant belonging to the *Fabaceae* family was studied and characterized at our laboratories by LC-MS, GC-MS and ICP-MS to identify the chemical species present. Since high level of polyphenols (in particular proanthocyanidin oligomers) was found, the extract was tested against the proliferation of cancerous cell lines, giving satisfactory results.

In order to identify what are the active species, different strategies dealing with the fractionation of the plant extract have been used. The significant active fractions against different type of cancerous cell lines have been analysed by micro liquid chromatography coupled with tandem high-resolution mass spectrometry. The analyses have been carried out by using MS/MS<sup>ALL</sup> with Sequential Window Acquisition of All Theoretical Fragment-Ion Spectra (SWATH) acquisition to obtain a comprehensive qualitative analysis with MS/MS confirmation. The study is still in progress, and a proteomic approach to understand the different mechanism characterizing the effect of the plant extract on healthy cells vs cancer cells is going to be carried out.

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**HIGH RESOLUTION MASS SPECTROMETRY COUPLED TO UHPLC AS A TOOL FOR THE UNEQUIVOCAL IDENTIFICATION OF ESTROGEN METABOLITES IN MILK**

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The coupling of ultra-high-performance liquid chromatography (UHPLC) with high-resolution mass spectrometry (HRMS) has been well received within the analytical community. Their resolution power and improved sensitivity, the increased robustness, extended dynamic range, easier mass calibration, and enhanced software handling capabilities, has made this coupling more attractive to a larger user base.

The use of HRMS coupled to chromatographic techniques offers among other the possibility to identify in an unequivocal way the presence of unknown compounds for which analytical standards are not available (non-targeted analysis). This fact is really useful when metabolites have to be identified. Moreover, the coupling with UHPLC, that offers an excellent resolving power, allows the simultaneous determination of quasi-isobaric compounds or structural isomers that with other chromatographic techniques are difficult to distinguish.

A representative example of the usefulness of UHPLC-HRMS with Orbitrap technology for the identification of unknown metabolites is the determination of estrogen metabolites in milk. Milk is known to contain naturally occurring estrogens such as estrone (E1), estradiol ( $17\beta$ -E2 and  $17\alpha$ -E2), and estriol (E3), and their glucuronated and sulfated forms. Although of natural origin, the presence of estrogens in milk has become a fact of great interest due to the potential health risk that their occurrence could suppose, especially regarding reproductive apparatus disorders.

Our research group has recently developed an UHPLC-ESI-QqQ methodology able to determine 13 estrogens both in their free and conjugated form in milk. Even if this methodology has been demonstrated very selective and sensitive for targeted analysis, there were individuated several unknown peaks that could not be identified. For this reason, it has been developed a new UHPLC-HRMS approach for the unambiguous identification of these unknown metabolites. The chromatographic separation has been carefully optimized using a last generation UHPLC system in order to obtain the complete separation of all unknown compounds, and the employ of high resolution full scan and data dependent experiments have allowed to obtain the accurate masses of the unknown compounds and their fragmentation pattern. In this way structural information has been obtained, which has allowed the unequivocal identification of estrogen metabolites in milk.



## LIGANDS IMMOBILIZED ON TRIACETYLCELLULOSE FILM TAPES FOR TRIVALENT AND BIVALENT METAL IONS SENSING

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We selected triacetylcellulose as solid phase and Dithizone and Alizarin Red S as metal indicators with the intent of building-up a probe for the simultaneous detection of trivalent and bivalent metal ions in water samples.

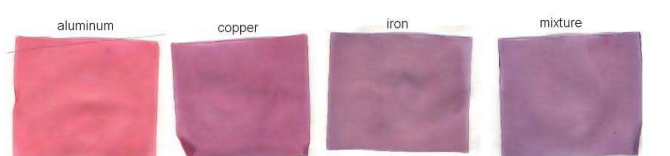
The transparent triacetylcellulose membranes were produced from photographic film tapes, previously treated with NaClO to remove coloured gelatinous layers. The lipophilic Dithizone was directly immobilized, while the water-soluble Alizarin Red S via ion pair with cetylpyridinium chloride (CPC), in both cases under very mild conditions [1, 2].

The final materials showed good mechanical properties and were characterized to establish their kinetics and thermodynamic properties through the usual experimental sorption profiles, for each metal and each membrane. The sorption isotherms confirmed the concentration of ligand on the membrane (independently measured from the release of the ligand in an appropriate solvent) and the sorption profiles as function of pH were in pretty good agreement with those expected from the formation constants reported in literature for the same metal- ligand systems in solution.

In the second step, the chromatic properties of the derivatized membranes were studied via spectrophotometric measurements of the solid phase, with the intent to find a proper model to predict, from the spectra obtained from the unknown solutions, the content of the metal ions in a mixtures.

The Dithizone based membranes were selected for Cu(II), Cd(II) and Zn(II), and the Alizarin Red S ones for Fe(III) and Al(III).

The model was applied on an external test set, with a satisfactory prediction. Tests on certified sample of milk and sewage sludge gave results within an error of 20 % .



**Figure 1** Alizarin Red S based membranes after contact with solution of only aluminium, copper and iron, and in the case of a mixture, respectively.

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**GROWTH INHIBITION OF *PSEUDOMONAS FLUORESCENS* BIOFILMS VIA ION BEAM SPUTTERED Ag/TEFLON COMPOSITE FILMS: A COMPARATIVE MORPHOLOGICAL AND SPECTROSCOPIC STUDY**

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The colonization of surfaces and interfaces by microorganisms leads to the formation of biofilms, i.e. an aggregate of bacteria embedded within a matrix of extracellular polymeric substance (EPS). A major function of biofilms is providing surroundings resistant to antimicrobials, giving rise to potential health and environmental problems [1]. In this perspective, biofilm growth inhibition is a crucial issue for preventing bacterial infections [2]. Metal/Teflon-like (Me-CF<sub>x</sub>) composites deposited via ion beam sputtering (IBS) are known as antimicrobial agents [3], whereby Ag-CF<sub>x</sub> thin films are considered novel materials with exceptional in-plane morphological and chemical homogeneity.

In this study, an Ag-CF<sub>x</sub> thin films with a metal loading of 25% was characterized spectroscopically and morphologically. Bacteria were then incubated onto a ZnSe ATR waveguide with the Ag-CF<sub>x</sub> deposited only onto IR inactive areas. Those regions were identified following a procedure reported elsewhere [4]. Thereby, real-time ATR-IR monitoring of *P. fluorescens* biofilm growth inhibition induced by the nano-antimicrobial coating was enabled. Few hours of contact were sufficient to inhibit the biofilm growth. These findings were corroborated by AFM imaging of bacterial samples incubated with Ag-CF<sub>x</sub> films deposited onto glass slides. Severe bacterial stress was induced by the composite antimicrobial material leading either to membrane leakage/collapse or to massive bacterial lysis as a function of incubation time.

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**SURFACE PLASMON RESONANCE IMAGING DETECTION OF  
FOODBORNE PATHOGENS BY USING PNA PROBES AND GOLD  
NANOPARTICLES**

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The detection of pathogens in food represents an essential requirement to ensure public safety and health [1]. Still today, conventional methods used to detect foodborne pathogens are laborious, time consuming and may suffer from low sensitivity. In this context, the use of optical biosensors have attracted great interest [2]. Surface plasmon resonance imaging (SPRI) [3] detection of nucleic acids has been shown to be performed with high sensitivity and selectivity [4]. In particular, peptide nucleic acids (PNAs) probes offer new possibilities in nucleic acid sequences biosensing and can be used to reveal pathogens with high selectivity and sensitivity [5]. Gold nanoparticles (AuNPs) have been used to amplify SPRI detected signals and to develop assays operating with enhanced sensitivity [6].

In this communication, a specific sandwich hybridization strategy to develop SPRI biosensors for the detection of *Staphylococcus Aureus* (*S. Aureus*) pathogen in food will be described. The sensing strategy involves the use of properly functionalized AuNPs conjugated to an oligonucleotide sequence complementary to the tract of the *S. Aureus* genomic DNA not involved in the hybridization with the SPRI sensor surface-immobilized PNA probe. Results show that the developed protocol can be applied for the detection of *S. Aureus* genomic DNA extracted from contaminated food.

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**Acknowledgements**

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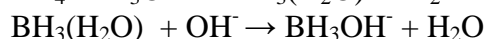
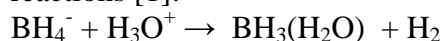
## INSIGHTS INTO THE CHEMICAL VAPOR GENERATION OF CADMIUM AT TRACE LEVEL

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Chemical vapor generation (CVG) of cadmium by aqueous boranes has been investigated by using continuous flow reaction system coupled with quartz tube atomizer and atomic absorption spectrometry, with the aim to clarify some of the mechanisms controlling the generation of volatile species. Experimental evidence collected in the present study indicates that  $\text{BH}_3\text{OH}^-$  is the most likely effective species in the generation of volatile Cd species. It can be synthesized on-line by quenching the acid hydrolysis of  $\text{BH}_4^-$  by NaOH, according the following reactions [1]:



The use of  $\text{BH}_3\text{OH}^-$  in alkaline conditions increases sensitivity of about a factor 2.2 with respect to  $\text{BH}_4^-$ , indicating an improved generation efficiency.

A further parameter controlling dramatically the sensitivity was the presence of dissolved oxygen in the reagents. Removal of oxygen from analyte and reductant solutions, by argon purging, resulted in a sensitivity improvement of about 8 fold and 6 fold by using  $\text{BH}_4^-$  and  $\text{BH}_3\text{OH}^-$  reductant, respectively. Oxygen gas added between gas-liquid separator and the atomizer hardly affects the sensitivity, indicating that the oxygen interferes mainly in the liquid phase, during the generation step of volatile Cd species. The use of  $\text{BH}_3\text{OH}^-$  under oxygen free conditions resulted about 13 fold improved LODs (about  $10 \text{ ng L}^{-1}$ , 3s). The use of additives as thiourea (up to 1%) in the presence of  $\text{Ni}^{\text{II}}$  ( $10 \text{ ng mL}^{-1}$ ), which are typically employed as signal enhancers in CVG of Cd [2], resulted in a marked signal depression for concentration of thiourea  $> 0.1 \text{ g L}^{-1}$ .

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## **LA-ICP-MS MAPPING OF THE SILVER DISTRIBUTION IN SKIN DURING WOUND HEALING**

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Silver nanoparticles (AgNPs) –containing dressings are increasingly being used in the treatment of wounds and skin burns. Recently we demonstrated that AgNPs can be massively released as agglomerates onto the skin, penetrate deeply into the dermis, enter into the fibroblasts by endocytosis, and accumulate to a remarkable amount into the cytoplasm.

In this work skin biopsies were collected from three different patients treated with AgNPs dressings. The samples, taken during the healing process, were analyzed by laser ablation coupled to inductively coupled plasma mass spectrometry (LA-ICP-MS) to map the distribution of carbon, phosphorus, sulphur and silver with a spatial resolution ranging from 5µm-100µm.

The analyses confirm that silver is released in the dermis during treatment. After the new epidermis is formed, silver released by the applied dressing does not seem able to cross the new epidermis and remains on the surface of the skin. No silver was observed in the subcutaneous adipose tissue. For the first time silver was detected in the vessel walls.

We concluded that silver is not able to cross the epidermis and the adipose tissue, and it is distributed to the organs via the blood stream due to its ability to penetrate into the vessels after release directly onto the dermis.

**LABEL-FREE SURFACE-ENHANCED RAMAN SPECTROSCOPY OF BIOFLUIDS: DIAGNOSTIC APPLICATIONS IN ONCOLOGY**

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Surface-enhanced Raman scattering (SERS) spectroscopy has recently raised interest for its potential in the field of diagnostics. Being portable and with quick responses, SERS is particularly appealing for point-of-care applications.

SERS spectra of biofluids (e.g. serum, urine) can be viewed as "partial metabolic fingerprints", which could be exploited for diagnosis [1]. Recent works by our group showed how SERS spectra of biofluids do indeed have the potential to be used for diagnosis of different types of cancer. Preliminary results showed how SERS can detect prostate cancer from urine samples with promising sensitivity and specificity [2], whereas both early and locally advanced breast cancer could be detected by SERS of serum.

Data analysis issues will be addressed as well, as a key aspect of such SERS-based diagnostic approaches is the application of chemometrics to build and validate predictive models.

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**THALLIUM CONCENTRATION LEVELS IN HAIR, URINE AND SALIVA IN A CONTAMINATED POPULATION IN THE NORTHWEST OF ITALY**

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Water-soluble thallium (Tl) compounds are highly toxic for most living organisms. Tl toxicity to mammals is higher than that of Hg(II), Cd(II) and Pb(II), because it chemically behaves as a heavy metal and because, due to its charge and size, it is an analogous of potassium. Thus, it has been notified as an important EPA priority pollutant. Thallium maximum contaminant level (MCL) in drinking water defined by EPA is 2 µg/L and 0.1 µg/L in China (CNS 2006) [1].

A recent study showed the presence of Tl at high concentrations (up to 9000 µg/L) in groundwater near Valdicastello Carducci (Italy). The contamination is supposedly due to acid drainage from abandoned mining areas. In September 2014 Tl contamination was also found in water intended for human consumption distributed in the same area.

We report here the preliminary results of a non-invasive population-based study that aimed to quantify the Tl levels in about 100 urine and 330 hair samples from the population of Valdicastello Carducci and Pietrasanta, Italy. Several saliva samples were also collected in order to explore this matrix as exposure indicator. All samples were analyzed by ICP-MS.

Tl values found in urine and hair samples were correlated with Tl concentration levels found in tap water in the living area of each citizen and with his/her habits (use of tap water both to drink and to cook or only to cook). The kinetics of decay of Tl concentration in urine samples was also investigated. About 50% of urine samples had a Tl concentration value above 0,5 microgram/L; about 70% of hair samples had a Tl concentration > 10 ng/g (2 ± 1 ng/g is the value of not exposed people). The high values of thallium found in hair samples suggest a long-term exposure.

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**SAMPLING AND CHARACTERIZATION OF MICRO- AND NANOPARTICLES FROM GAS TUNGSTEN ARC WELDING (GTAW) FUMES**

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In the working environment, several sources of metal nanoparticles with relevant toxicological effects can be found. Among these sources, the welding fumes (WF) are probably the most interesting one both from a chemical and toxicological point of view. The high temperatures used in welding operations originate micro- and nanoparticles represented by metal oxides, unoxidized metals and compounds, such as fluorides and chlorides. These kind of particles with a large surface-to-volume ratio have well-documented effects on health. Characterizing dimensions, shape and composition of WF particles is important to better understand the physicochemical parameters involved in their generation and in the attempt to clarify which aspects are responsible for their toxicity.

In this study, two different real sources of GTAW fumes, collected in an automotive plant, were characterized by TEM-EDS. Three indoor sampling zones were set: in proximity of the automatic welder arm; next to the operator performing manual GTAW; in a zone of the factory far from the exposure source as a reference background. In each sampling zone, three air sampler pumps were set to a flow of 2.2 L min<sup>-1</sup> and connected each one to a personal cyclone sampler for respirable dust containing a 5 µm filter (cellulose) in the filter cassette. Under the 5µm filter, two TEM copper grids were placed in order to collect the particle fraction with dimensions <5 µm.

The particles sampled during the automatic process have the smallest diameter in comparison with the other two sampling zones, and a crystalline composition consistent with the bulk material. The particles found in the second sampling zone, in comparison with those sampled in the first zone, showed a larger diameter and a different morphology. Moreover these particles were mostly aggregates with a significant percentage of chromium. The particles found in the third zone were consistent with the atmospheric particulate matter of natural origin. These results generate the hypothesis that even the same kind of welding process produces different classes of fumes depending on factors like the lifetime of the welding process.



# Posters

## USE OF LYSO-PHOSPHOLIPIDS AS MARKERS OF THERMAL TREATMENTS EFFECTED ON COMMERCIAL MUSSELS: A LC-ESI-MS STUDY

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Due to significant intra-continental trade flows and to a relevant import from extra-EU countries, like Chile or New Zealand [1], mussels commercialized in Europe are often involved in mid/long range transportation. Appropriate storage conditions have to be thus implemented to assure the product quality and safety. They include refrigeration and freezing after glazing (a special procedure performed on unwrapped, cooked mussels to generate a protective thin ice layer around the meat), according to storage time [2]. European regulations (853/2004, Annex III) are quite stringent on these procedures, especially when live mussels are traded. Nonetheless, modifications (storage under relatively cold, recycling sea water) or even violations (prolonged storage at room temperature) of the regulations are often observed, especially when small retailers are involved. The potential of mussel *Lyso*-phospholipids (LPLs) arising from major phospholipid classes (phosphatidylcholines and phosphatidylethanolamines) as markers of thermal treatments has been assessed in our laboratory using an analytical method based on hydrophilic interaction liquid chromatography (HILIC) and ESI-MS and MS/MS detection [3]. In the present communication the correlation between LPLs and mussel thermal histories, evaluated on a statistical basis on commercial samples, will be discussed. In particular, it will be emphasized that refrigeration for a reasonable time (up to 4 days), as prescribed by EU regulations, is safe both for mussel vitality and for quality (expressed in terms of PL integrity). On the contrary, freezing (without glazing)-thawing, on one side, and storage at warm room temperatures, on the other, may result in a remarkable increase of specific LPLs, indicating a significant deterioration of product quality.

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## **MULTIVARIATE CLASS MODELING TECHNIQUES APPLIED TO MULTIELEMENT ANALYSIS FOR THE AUTHENTICATION OF MEAT PRODUCTS OF “SUINO NERO DI CALABRIA”**

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The “Suino Nero di Calabria” (Black Pig of Calabria) is an ancient breed typical of southern Italy reared in the wild and fed with natural products such as acorns, chestnuts and cereals. Its meat gives high quality products such as ham, lard, pancetta, and sausages. Authentication of food products may represent a key point for farmers and producers. In fact, from an economic point of view, the check of geographical origin is fundamental to prevent unfair competition that can eventually affect the regional and even national economy. Moreover, origin should guarantee quality, organoleptic, and nutritional characteristics for consumers.

Our research group has demonstrated that the multielement profiling subjected to a suitable statistical treatment can be successfully used in the determination of the geographical origin of several foodstuffs [1].

In this presentation, the capability of multielement profiling as a marker for the authentication of the “Suino Nero di Calabria” products (ham, pancetta, and lard)” is evaluated. The multielement determination was performed by ICP-MS on samples supplied by certified “Suino Nero di Calabria” producers and on samples came from areas outside Calabria.

A proper application of chemometric pattern recognition strategies is required for the verification of food-authenticity claims. Although the classification techniques (especially LDA) are very frequently used in authentication studies, these approaches are not the best approach for the verification of food geographical origin and could be really suitable only to assign an origin to a sample without label. On the other hands, class-modeling permits the construction of a multivariate enclosed space of a single class of interest, to verify whether a sample is compatible or not with the characteristic of that class. Therefore, the statistical approach for the data treatment was based on class-modeling techniques. In addition to the classical modeling approaches commonly applied in chemometrics (soft independent modeling of class analogy, SIMCA and unequal dispersed class, UNEQ), other two methods have been applied in the present study: potential functions (PF) and multivariate range modeling (MRM).

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## NMR STUDY OF THE MICROWAVE-ASSISTED EXTRACTS OF *AZADIRACHTA INDICA* LEAVES

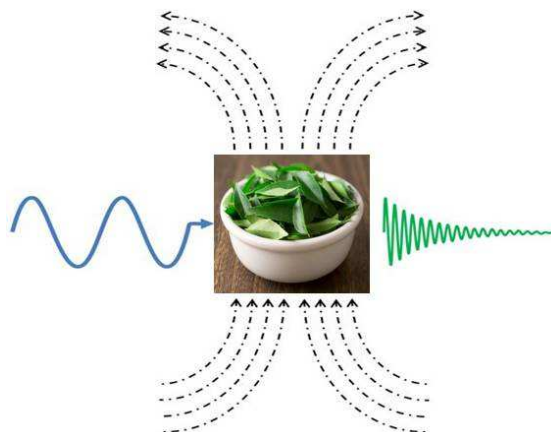
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Neem (*Azadirachta indica* Juss., Meliaceae) leaves have been widely proposed as a traditional medicine and many bioactive compounds have been isolated, but no NMR fingerprint of both the microwave and conventional extracts has been reported so far. Taking into account the higher variability of the content of the plant constituents, which is probably influenced by the environment and the crop production technology, a proper analytical method is important for monitoring the quality of the product. Pursuing our research in this field [1,2], we carried out two different extraction techniques evaluating at 40 °C for 10, 30 and 60 minutes the recovery of a large range of metabolites by using three solvents (methanol, chloroform and acetone) in order to obtain an untargeted analysis of the Neem leaves content by NMR spectroscopy.



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## ASPHODELINE ROOTS AS A NEW SOURCE OF NATURAL COMPOUNDS: EVALUATION OF ANTIOXIDANTS, ENZYME INHIBITORS, AND CHEMICAL COMPOSITION.

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Plant-based foods have become attractive for scientists, food producers, and for their often-valuable biological activities as “*functional foods*”. Positive effects related to their consumption as dietary supplements are due to the presence of natural occurring secondary metabolites. In this context, studies on these products are fundamentals for natural and safely food ingredients evaluation, and for quality control analyses in order to avoid adulterations and sophistications.

The aim of this study was to evaluate root extract of eight Asphodeline species in terms of antioxidants, and enzyme inhibitors activities, and phytochemical content.

Anthraquinones chemical fingerprints were obtained using validated HPLC procedure [1], while total phenolics and flavonoids contents, and enzyme inhibitors activities were obtained using validated spectrophotometric assays.

Data show that Asphodeline roots can be considered as a new source of natural compounds and can be used as valuable dietary supplement [2]. Some differences related to biological activities can be inferred to other phytochemicals that can be considered in the future for their synergic or competitive activities.



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**TARTARY BUCKWHEAT AS A SOURCE OF NUTRACEUTICALS:  
POLYPHENOL DETERMINATION BY PRESSURIZED LIQUID  
EXTRACTION AND ULTRA HIGH PRESSURE LIQUID  
CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY**

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Buckwheat (*Fagopyrum* spp.), member of the Polygonaceae family, is not only a gluten-free pseudocereal, therefore suitable for coeliac people diet, but it also contains bioactive compounds with health protective effects, that make it a potential ingredient for functional foods [1]. In particular, buckwheat represents a good source of flavonoids (rutin, quercetin, orientin, isoorientin, vitexin, isovitexin) and among these compounds, rutin (quercetin-3-O-rutinoside), exhibits hypotensive effect, antihemorrhagic and antioxidant activities.

Two major species of buckwheat are cultivated: the common buckwheat (*Fagopyrum esculentum* Moench) and the tartary buckwheat (*Fagopyrum tataricum* Gaernt), the latter has higher levels of rutin (up to 100 times) than common buckwheat [2].

The aim of the present work, carried out within the activities of the BUCKFOOD Project (MiSE Industria 2015, Nuove Tecnologie per il Made in Italy), is the characterization of some tartary buckwheat varieties to determine their polyphenol profiles.

An extraction method was developed by pressurized liquid extraction, (PLE), in order to achieve the highest yield of rutin, employing one variety as *in-house* reference material. The optimized extraction conditions by PLE (temperature, pressure, solvent extraction mixture, number of cycles and flush volume) were applied to three tartary buckwheat varieties (namely Donan, Golden and Ishisoba) and the extracts were analysed by LC-MS/MS analysis using a UHPLC-ESI-Q-TOF system to obtain polyphenol profiles.

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## **A NEW METHOD BASED ON A CORE-SHELL COLUMN FOR THE DETECTION OF SULPHONAMIDES IN MILK BY A CONVENTIONAL HPLC-DAD SYSTEM**

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Sulphonamides (SAs) are drugs, derived from sulfanilic acid (p-aminobenzenesulfonic acid), which act as bacteriostatic agents. The widespread and often uncontrolled use of SAs in veterinary practices for prophylactic and therapeutic purpose contribute to their potential increasing presence in farm animals and consequently in food intended for human consumption. This is of significant concern because of the possibility to produce antibiotic resistance, allergic reaction in hypersensitive individuals and their potential carcinogenic character. In order to increase the food safety, the European Union has established a maximum residue limit of 100 µg/kg for the sum of all SAs in milk, tissues and muscle (Commission Regulation (EU) No 37/2010). Several methods have been proposed to determine SAs in different matrices using traditional columns with 5 µm particles which require running times around 30-60 min to analyze 7-18 analytes. In order to obtain fast analysis and improve the chromatographic efficiency, a new method based on the use of a 4.6 ID mm x 75 mm column packed with core-shell particles on a conventional HPLC-DAD system has been applied to the determination of SAs in milk. Since the high performance liquid chromatographs were not designed for the core-shell packed column, chromatographic conditions, such as the mobile phase flow rate, injection volume and gradient elution, have been studied to achieve the best compromise between separation efficiency of SAs and chromatographic run time. The optimized method, able to quantify 13 SAs in less than 9 minutes, has been validated according to the European Decision 657/2002, as established for analyses of drug residues in food. Mean recoveries of the 13 SAs for raw milk ranged between 55% and 86% at the MRL level, and RSD % resulted lower than Thompson and Horwitz RSD % reference values.

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## VALIDATION OF AN HPLC/FLD METHOD FOR AFLATOXIN B<sub>1</sub> DETECTION IN ANIMAL FEEDSTUFFS

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Aflatoxin B<sub>1</sub> (AFB<sub>1</sub>) has been associated with several toxic effects in animal and human health including carcinogenic, mutagenic, teratogenic and immunosuppressive activity. Dairy animals consuming AFB<sub>1</sub> contaminated feeds accumulate, in the milk, a thermo-resistant hydroxylated metabolite of AFB<sub>1</sub> known as aflatoxin M<sub>1</sub>. The EU limits for AFB<sub>1</sub>, in animal feeds range from 5 to 20 µg/kg depending from animal species, age and lactation (Regulation (EC) No.574/2011). According to European Food Standard Agency, the monitoring of the presence of AFB<sub>1</sub> in the raw materials and feedstuffs through reliable and validated methods, should be encouraged in all EU member states. Analytical methods suitable for aflatoxins official control need to comply with legislation (Regulation (EC) No.882/2004) and with commonly accepted criteria (ISO 17025/2005). However, taking in to account the complexity and variety of animal feed matrices, a validation protocol specifically designed for the analysis of aflatoxins in feed does not exist. An in-house validation model, in agreement with UNI CEN/TR 16059-2010 and the recent Eurachem Guideline [1], has been proposed for a method based on HPLC/FLD already developed in our laboratory [2]. Method has been validated using 3 different blank samples of animal feed (for dairy cattle, lambs and piglets) spiked respectively at 5-10-20 µg/kg. Intra-laboratory accuracy was estimated in two different analytical session obtaining RSD% values ranging from 5.34-3.04 and recovery values from 62.3 to 69.7%. Method selectivity was tested on 40 feed samples of different species. Linearity was checked by Mandel test injecting 4 standard solutions at concentration of 1.25-2.50-5-10-20 µg/l. LOD and LOQ values of 0.4 and 1.3 µg/kg were largely lower than legal limits. Furthermore, measurement uncertainty has been carefully evaluated. In addition, ruggedness studies have been performed to extend the method applicability to complete and complementary feeds for other animal species.

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## FAST AND RELIABLE DETERMINATION OF PHTHALATES IN COFFEE

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Coffee is one of the most frequently consumed beverages all over the world [1]. Similar to other foodstuffs, this beverage can be contaminated by plasticizers, particularly phthalates (PAEs) [2] during production or food chain transfer of these compounds.

Since many years this research group has developed a rapid and efficient analytical procedure for analyzing seven phthalates (DMP, DEP, DiBP, DBP, BBP, iBcEP, DEHP) in different matrices. This communication would like to investigate PAEs in coffee using a methodology based on dispersive liquid-liquid microextraction followed by GC-FID/MS. Actually, we modified the procedure using ultrasound and vortex. In this way, the method analyzes real samples without long and tedious analytical steps and simultaneously reaching high quality data. Compared to previous papers the salt effect is investigated and discussed: no salt was added to the solution before processing for the PAE investigation. The matrix effect is also another interesting point discussed: different vortex times were tested before setting the final procedure. Among different solvents, 400  $\mu$ L of heptane were used for extraction: after ultrasound and vortex procedures 1  $\mu$ L was injected in GC-MS system. Analytical parameters such as recoveries (ranging between 88-102 %), Limit of Detections and Limit of Quantifications, Enrichment Factors (average value 280), repeatability (below 9 %) have been studied. Finally, the entire procedure has been applied to real samples available on the Italian market: different coffees as powder, pot or capsule have been analyzed. DMP was the only PAE determined in all the samples whereas their distribution is not homogeneous. It is interesting to note that the levels determined are not considered worrying for the human health.

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## **MICROARRAY ASSAY AS A SCREENING METHOD FOR THE DETERMINATION OF PROCESSED ANIMAL PROTEINS IN FEED**

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Recent crises in the feed sector such as bovine spongiform encephalopathy (BSE) have highlighted the need for more stringent food quality control, which should include determination of processed animal proteins (PAPs) in feed [1].

EC Regulation 999/2001 governing the use of PAPs in feed has been amended several times introducing a ban on almost all PAPs in animal nutrition. A new European Regulation has recently been passed (Commission Regulation (EU) N 56/2013) authorizing the use of *non-ruminant* PAPs in feed for aquaculture.

Consequently, species-specific detection and detection of groups of species such as ruminants is required according to European legislation dealing with the safe use of animal products in animal nutrition [2]. Therefore, there is a strong need for ruminant specific test in order to establish whether traces of ruminant proteins are present in feed [3].

As described in the recent European Regulation (Commission Regulation (EU) N 51/2013), the official method of analysis includes light microscopy and real time PCR. Depending on the type of feed being tested, these methods may be used, within one single operational protocol, either on their own or combined together in accordance with the standard operating procedures established by the EU reference laboratory for animal proteins in feeding stuffs (EURL-AP).

In this work, a microarray approach allowing for the simultaneous detection of ten different species (bovine, porcine, goat, sheep, poultry, buffalo, chicken, turkey, horse/donkey and fish) was proposed as a screening method for the qualitative detection of PAPs in feed. Microarray assay is currently used for detecting the adulteration of meat to fight against deliberate substitution of one meat species by a cheaper one. This method uses two kinds of molecular biology technologies, polymerase chain reaction and hybridization.

For the development of the method a commercial kit was used and feed samples by a proficiency test were analyzed. The sensitivity of the assay was measured and its reliability too, showing a good accordance with requests of European legislation except for the presence of fishmeal.

Through the microarray it was possible the identification of animal species for samples that were found to contain terrestrial animals traces by microscopy whose limitation is the lack of animal species specificity.

It is thus concluded that preliminary data of microarray technology, evaluated in this study, demonstrated animal specificity and this technique could be a viable screening method for routine detection of PAPs especially in feed for aquaculture, thanks to high sensitivity shown in bovine DNA detection, higher than that for

fish's DNA. It allows the preliminary use of only one technique rather than two combined.

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**DETERMINATION OF YLOID IN SOIL ➔ OLIVE OIL FOOD CHAIN (OLEA EUROPEA) BY ICP-MS TECHNIQUE: A GEOGRAPHICAL CHARACTERIZATION OF FOOD PRODUCTS? A CASE STUDY. (III)**

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The rising importance given from legislators and consumers to provenance of food purchased and/or eaten, in last years motivated several researches to identification of the geographical origin of food. The olive oil plays a fundamental role in the Mediterranean diet. Traceability of olive oils is relevant not only in assessing their origin, but also in protecting against frauds. The knowledge of a chemistry relationship between the soil and the agricultural products is an important tool for the quality assessment of food. YLOID (Y, La and Lanthanoid) have recognized as very useful tracers due to their generally coherent and predictable behavior. This behavior can also be applied to explain the mechanisms of element intake by plants. Current knowledge suggest no preferential sorption of any element in overall root samples as well as in epigeal samples of several plants. Taking into account of our previous works carried out on grapevine – soil system [1, 2], we applied the same technique to evaluate and trace the YLOID distribution in *Olea europea* olive oil – soil system. Sampling of soil and olives was carried out in the experimental farm “Campo Carboj” located in Menfi (AG, Sicily) where are present several *Olea* cultivars of different Mediterranean countries. Different types of olive oil, were obtained by grinding the olives samples. The aim of the research was to observe if olives of different cultivars grown on the same soil and their oils could reproduce the same YLOID distribution. In this study, the YLOID amounts and distribution in olive oil - soil system were determined and relationship Yb vs La and/or the pattern of distribution of YLOID were calculated. The obtained results in terms of lanthanides were critically discussed based on the different amounts found.

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**LACTOFERRIN CONTENT AND TOTAL ANTIOXIDANT CAPACITY DETERMINATION IN FOOD INTEGRATORS, ANIMAL MILKS AND POWDERED MILK.**

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Lactoferrin is an iron-binding glycoprotein of the transferrin family, which exerts an important function for in host defence; its modulation of iron metabolism has been studied and elucidated as its functionality is related to its strong iron binding properties. Lactoferrin exploits various biological effects: antibacterial, antiviral, antitumor, antiatherogenic and immunoregulatory functions [1]. In addition several studies have demonstrated an antioxidant activity of lactoferrin [1]. These researches point to the existence of specific binding sites for lactoferrin on the erythrocyte cell membrane. In practice, lactoferrin, as a final acceptor for the electron carried by the trans-membrane electron transporting chain, could also influence the state of the intracellular antioxidative protection of the red cell. In view of its many therapeutic properties, but above all owing to its antimicrobial, antioxidant and immunoactivity properties, lactoferrin may therefore be considered an essential component of mother’s milk (both animal and human). It has therefore been used as a deliberate additive in infant formulas and similar food products. However, recently also food supplements for adults containing lactoferrin have appeared on the market. Recent experimental results support the proposal that oral supplements of bovine lactoferrin may be a useful adjunct in the modulation of immune activity, in particular T-cell activation and antioxidant status. Our research team in recent years has developed both an excellent immunosensor for the determination of lactoferrin concentration in milk and milk derivatives, and an electrochemical superoxide dismutase biosensor for measuring total antioxidant capacity (TAOC). Using these two sensors we simultaneously measured lactoferrin concentration and antioxidant capacity in three food supplements sold in drugstores as well as in cow, goat and powdered milk and in yoghurt. It was not always possible to prove a direct relation between lactoferrin concentration and (TAOC), as one or two other molecules with a known antioxidant capacity are present in food supplements. However, the lactoferrin content was clearly shown to contribute to total antioxidant capacity in both food supplements and various milk and milk derivative samples. It also proved possible to perform a simple fast check of the food supplements tested and compare the lactoferrin concentration declared by the manufacturers with the actual test results.

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**A NEW GC-FID METHOD FOR THE DETERMINATION OF MAIN SACCHARIDES IN MILK AND ITS APPLICATION TO VERIFY THE “LACTOSE FREE” CONDITION IN DIFFERENT DAIRY FOODSTUFFS**

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A new GC method for the determination of simple carbohydrates profile in milk of different origins and dairy products has been developed and validated through analysis performed on commercial cow milk samples.

The composition of raw cow milk determined the choice of lactose, glucose, galactose, *myo*-inositol and tagatose as analytes, the last one as a marker of possible high thermal treatments.

The developed method requires a pretreatment step of samples, necessary to remove fats and proteins from the whey, followed by a derivatization step to make samples suitable for the GC analysis.

The entire procedure was validated through the determination of various parameters for all the studied analytes, like linearity ranges, detection (LOD) and quantification (LOQ) limits, precision and bias.

The proposed method was applied to commercial products as UHT skim type and UHT lactose free skim type cow milks.

Through the optimization of the pretreatment step, the developed procedure was used to evaluate the lactose content in Pecorino cheese samples, supplied by The Consortium for the Protection of Pecorino Romano DOP Cheese, and, afterwards, in different types of ricotta samples produced after an enzymatic treatment of the raw milk with  $\beta$ -galactosidase.

The experimental results allowed to get the average carbohydrates composition of UHT skim type milk samples, the glucose and galactose concentrations of UHT lactose free skim type milk and a lactose content under the LOD value for cheese and ricotta samples.

**PRELIMINARY RP-HPLC APPROACHES TO THE CHARACTERIZATION OF NUTRACEUTICAL COMPONENTS IN *STEVIA REBAUDIANA BERTONI*'S LEAVES**

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*Stevia rebaudiana Bertoni* is a branched shrub of the Asteraceae family native to the tropical areas of Northern and Southern America, nowadays widespread in many regions of the world. It has a significant economic value due to its high content of natural, dietetically valuable sweeteners in its leaves. They consist in steviol glycosides as stevioside and rebaudioside A, the most abundant among more than 30 compounds recognized in different *Stevia* genotypes [1]. The composition of *Stevia* leaves is extremely variable and includes nutritional and functional components as vitamins, minerals, protein and amino acids, polyphenols, lipids and carbohydrates.

The quali-quantitative characterization of these classes of compounds may be a useful tool to differentiate and valorize plants grown in various regions and conditions. This approach allows the individuation of promising genotype in terms of sweeteners' yield and/or nutraceutical value.

In this context our group has begun a research project to acquire optimized RP-HPLC procedures for the determinations of steviol glycosides, free amino acids and hydro-soluble vitamins in *Stevia* leaves. At this moment extraction procedures for the three classes of analytes of interest and the chromatographic conditions for their separation (stevioside, rebaudiosides A and C and dulcoside A, among the glycosides; 17 amino acids; 6 vitamins) are performed and preliminary applied to a sample from Perù, while the evaluation of the validation parameters of the whole methods, as linearity ranges, precision, bias and detection and quantification limits, are determined or are going to be acquired.

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## VALIDATION OF A CONFIRMATORY METHOD FOR THE DETERMINATION OF QUINOLONES IN EGGS BY LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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Quinolones are broad-spectrum antibiotics widely used for food producing animals, forbidden in laying hens producing eggs for human consumption. Several chromatographic techniques have been used for the determination of quinolones in eggs [1]. The aim of this study was to validate a confirmatory method for the simultaneous determination of 11 quinolones (ciprofloxacin, danofloxacin, difloxacin, enrofloxacin, flumequine, lomefloxacin, marbofloxacin, norfloxacin, nalidixic acid, oxolinic acid, sarafloxacin) in eggs according to Commission Decision 2002/657/EC.

The analytes were extracted using a mixture of 0.1% methanol/metaphosphoric acid and purified by solid-phase extraction on OASIS HLB (3 mg/60 ml). The LC-MS/MS analysis was carried out by a triple-quadrupole mass spectrometer, selecting one precursor ion to two products ion transitions for each analyte.

The specificity was assessed by the analysis of 20 blank eggs. The calibration curve was linear in the range 0–2000 pg injected ( $R^2 \geq 0.990$ ). Linearity was evaluated for ciprofloxacin, danofloxacin, enrofloxacin, lomefloxacin, marbofloxacin, norfloxacin, and sarafloxacin using internal standard (norfloxacin-d5). For all the analytes, the precision in eggs spiked at 5, 10 and 15  $\mu\text{g}/\text{kg}$  was satisfactory giving relative standard deviation values in the range 2.1–15.9% (within day) and 3.5–20.7% (between days). Regarding to trueness, the recovery ranged from 95 to 101.6% and complied with the legislation requirements. The  $\text{CC}\alpha$  and  $\text{CC}\beta$  values ranged from 5.6 to 7.4  $\mu\text{g}/\text{kg}$  and from 6.2 to 9.9  $\mu\text{g}/\text{kg}$ , respectively. Ruggedness for minor changes was evaluated according to the Youden approach. The method described is very robust and can be used for a sensitive detection and accurate quantification of quinolones in eggs.

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## **FTIR COUPLED WITH PLS-DA AGAINST FRAUDS: THE CASE OF HEAVY-SALTED DESALTED AND LIGHT-SALTED COD FILLETS**

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Cod (*Gadus morhua* L.) is a widespread white fish. In the Mediterranean countries, it is commercialized mainly as salted cod with different moisture content depending on the extension of the drying step [1].

Different salting process can lead to very different attributes of the final product, however no analytical method has been proposed to discriminate samples salted with or without the use of brine.

Vibrational spectroscopy methods, such as NIR and FT-IR, are fast and easy techniques, that can be used with minimal sample preparation and have been reported to be effective, coupled with chemometric data processing, particularly for food authentication issues [2].

In this work, the use of Fourier transform infra-red (FTIR) spectroscopy has been proposed in order to discriminate heavy-salted desalted (HS) cod samples from light-salted (LS). The method take advantage of Horizontal Attenuated Total Reflectance (HATR) FTIR to record cod loin samples spectra in the range 4000-650  $\text{cm}^{-1}$ . Cod loin samples are homogenised before analysis. Spectral data were then processed with partial least square discriminant analysis (PLS-DA) in order to discriminate the two analysed classes (HS and LS).

Different sources of variability of the sample were considered (such as packaging, storage time, producers, region of origin and freezing processes). A total of 258 samples were analysed. Both cross validation (CV) and external validation were performed in order to evaluate the discriminant ability of the method. 100% of the samples were correctly assigned in CV in any case, while for external validation data set, the final proposed model showed from 91 to 98 % of correct assignation. Robustness of the method has also been evaluated. The proposed method is a fast, cheap and “green” way to discriminate against frauds for cod production.

Authors wish to thank the Norwegian Seafood Research Fund SALDICOD project for financial support.

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## **DETECTION OF COFFEE POWDER ORIGIN BY ELECTRONIC NOSE AND GC-MS ANALYSIS**

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In the last years, the use of oligopeptide modified piezoelectric sensors has been demonstrated to be a very useful tool for many different applications. Gold electrodes on quartz crystal microbalances (QCMs) resulted particularly useful to immobilise peptides via self-assembled monolayer, using cysteine as terminal amino acid or, alternatively, a thiolated spacer.

More recently, the use of gold nanoparticles (AuNPs) modified with oligopeptides as QCMs surface modifying agent has been proposed (e.g. [1]). Encouraging results have been obtained due to the ease of derivatisation, high number of possible configuration and possibility to design via molecular modelling the ligands.

In this work, an application of a AuNP-peptide based sensors array on coffee powder samples is presented. Illy SpA (Trieste, Italy) kindly supplied Coffee powder samples. Five different kinds of samples were analysed (they were all commercial product from Illy SpA). Three coffee powders were from a single geographical origin (Costa Rica, Colombia and India – commercial name: Illy Monoarabica). One kind was a blend of coffees from nine different countries (commercial name: Illy Espresso) and the fifth was the same as the "Illy Espresso" but after decaffeination (obtained by industrial process with supercritical CO<sub>2</sub> – commercial name: Illy Deca). All samples were analysed on a TEN 2011 (Tor Vergata Sensors Group – Rome, Italy) e-nose apparatus equipped with 20 MHz QCMs. The sensors surfaces modified with seven GNP-peptides (Thioglycolic acid, Glutathione, Cys-Ile-His-Asn-Pro, Cys-Ile-Gln-Pro-Val, Cys-Gly, Cys-Arg-Gln-Val-Phe, Cys). The peptides were selected according to their chemical and physical properties. E-nose data were compared by GC-MS analytical data. Sensors arrays data showed the ability of multivariate statistical analysis on electronic nose and GC data to separate samples according to the geographical origin. GC-FID/FPD data for geographical discrimination was also tested with good results. With both techniques Colombia and Costa Rica samples showed a partial overlapping while India was well separated. It is worth noting that the not completely separate geographic area were the closest.

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## **INORGANIC COMPOSITION AND RAMAN SPECTROSCOPY AS NEW METHODS FOR THE IDENTIFICATION OF ANIMAL MEALS RESIDUED IN FEED.**

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Our study is aimed at evaluating the possibility of using inorganic composition and Raman spectroscopy as possible alternative methods of analysis for the individuation and characterization of Processed Animal Proteins (PAPs) in animal feeds.

The official analysis method approved by European Commission is based on optical microscopy [1], and on Real Time PCR. However, both methods present some drawbacks, (e.g. high staff specialization). Particularly, microscopy does not permit the identification of animal species present in feed. PCR methods are specific and sensitive in nature [2], but they are not able to distinguish between allowed and not allowed ingredients (e.g. Milk versus PAP). Many other techniques, as infrared microscopy, immunoassay methods, chromatographic and mass-spectrometry, were just evaluated as possible alternative methods. All these methods show advantages and limitations [3].

Four types of pure PAPs, namely bovine, swine, poultry and fish-based PAPs, have been analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES) and a FT-RAMAN spectrometer. All the procedure steps (samples pretreatment and analysis) and all the parameters and conditions were considered and optimized.

The application of multivariate chemometric techniques to the experimental results allowed us to determine the identification capability of the two techniques, to identify correlations among the variables and to reveal similarities and differences among the different species.

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## DETERMINATION OF OLIVE OIL ACIDITY: A NOVEL ELECTROANALYTICAL APPROACH

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Free fatty acids (FFAs) content in olive oil is a key parameter routinely determined to classify and/or assess the quality, the freshness, and the economic value of the final product available on the market. The official method, suggested by ECC Regulation, for the quantification of the olive oil acidity - expressed as mass percentage of free oleic acid -, is a classical acid/base volumetric titration, performed in non-aqueous solvents [1]. The procedure is simple, but very slow, laborious and organic solvent consuming. Considering the large number of routine measurements necessary for marketing purposes, the development of fast, simple, low-cost, solvent-free and reliable instrumental analytical methodologies for quantifying the olive oil acidity is a task of great interest.

To this purpose, in the present study an electroanalytical strategy for a direct evaluation of the acidity in olive oils is presented. The experimental conditions for exploiting the reduction process of the acidic species present in this food matrix were defined and optimised, under both deoxygenated and oxygenated conditions, taking as acid probe the oleic acid (OA), which is the prevailing long-chain FFA component of olive oil. Oil samples were prepared by adding, as supporting electrolyte, the room temperature ionic liquid (RTIL) trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl) imide ( $[P_{14,6,6,6}]^+[NTf_2]^-$ ), that is soluble in vegetable oil and enhance the matrix conductivity [2,3]. The measurements were performed in a 2 mL glass vial as electrochemical cell, using a 12.5  $\mu\text{m}$  radius Pt microdisk as working electrode. By applying a properly optimised chronoamperometric setup, reliable acidity data in some extravirgin, virgin, and lamp olive oil samples were found. The results obtained indicates that the electrochemical procedure developed can be advantageously exploited as a fast, low-cost and solvent-saving analytical tool for the determination of olive oil acidity.

*Financial support from PRIN 2010-11 prot. 2010AXENJ8, is acknowledged.*

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## A NOVEL ANALYTICAL STRATEGY FOR THE ASSESSMENT OF TRACE HEAVY METAL CONTAMINATION IN OLIVE OILS

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Trace heavy metals dangerous to human health, as Pb, Cd or Cu, can be present in olive oil because of contamination from soil and fertilizers, production or storage procedures, or exposition of the olive plants to vehicular and industrial emissions [1]. This problem has led to increasing interest in the development of sensitive and accurate analytical methods to monitor trace levels of these elements directly in edible oils, characterized by a high viscous organic matrix where traditional analytical techniques can hardly be applied without strong and time-consuming sample pretreatments.

To this aim, in this work a novel analytical approach combining electrochemical and inductively coupled plasma mass spectrometric (ICP-MS) measurements is proposed.

The experimental conditions for the voltammetric analysis in such low-conductive food matrix were defined taking lead as target analyte. Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl) imide ( $[P_{14,6,6,6}]^+[NTf_2]^-$ ), a room temperature ionic liquid (RTIL) soluble in vegetable oil, was used as supporting electrolyte [2]. The measurements were performed in a 2 mL glass vial, using a 10  $\mu$ m radius Pt microdisk or a glassy carbon ( $r=1.5$  mm) as working electrodes.

For the development and validation of the analytical procedure, standard reference solutions of lead were produced by galvanostatic dissolution of a bar of high-purity Pb directly in the pure RTIL. Varying the dissolution time, a set of  $Pb^{2+}/[P_{14,6,6,6}]^+[NTf_2]^-$  standards at concentration between 10 and 200 mg L<sup>-1</sup>, calculated by the Faraday law, was prepared. ICP-MS analysis of  $Pb^{2+}$  standards, after mineralization in a microwave unit by a digestion procedure properly set up, validated the method.

The strategy proposed here for the determination of Pb content in olive oils consists in the following steps: 1) metal preconcentration onto a thin Pt coil directly from the oil sample mixed with RTIL; 2) potentiostatic re-oxidation of the metal at +1.5V in 10% HNO<sub>3</sub> solution; 3) quantification by ICP-MS or voltammetric measurements in the acid solution obtained by step 2). The experimental results are presented and discussed.

*Financial support from PRIN 2010-11 prot. 2010AXENJ8, is acknowledged.*

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**SPME-GC-qMS AND SPME-GCxGC-TFM-TOFMS  
CHARACTERIZATION OF VOLATILE COMPOUNDS OF  
AUTOCTONOUS WHITE WINES FROM THE COLLIO AREA**

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The Collio is a vineyard area near Gorizia in Italy and close to the Slovenian border, renowned for excellent white wines. In this research we characterize three wines – namely Friulano, Ribolla Gialla and Malvasia Istriana – for their volatilome/VOCs qualitative and semi-quantitative profiles in order to identify *aroma* features of the different species. After optimization of instrumental parameters and derivatization of wine samples with PFBHA, HSSPME–GC–qMS was performed allowing the identification of 40 compounds, with abundance of aldehydes, esters and ketones. A pool of compounds was common and very similar in level to all the wine varieties, while Friulano presented relatively high concentration of some ketones and one ester while Ribolla Gialla had low values of some heavy esters. All these and other features can be highlighted by a Principal Component Analysis of the data set. The compounds with highest loadings on the first components are known to provide specific fruity aroma. More, focusing on Friulano wine, the composition of VOCs from Collio was compared with those of other areas from Friuli Venezia Giulia region, allowing a first identification of typical features of different regional wine production zones. An abundance of longer chain esters and aldehydes characterizes the Collio Friulano's versus those of other areas, richer in pentanal. An improvement in selectivity and sensitivity is allowed by SPME Total Flow Modulation GCxGC-TOFMS, highlighting the presence of compounds at low concentration but with significant odor threshold.

**SIMULTANEOUS DETERMINATION OF VITAMINS AND CAROTENES BY ON-LINE COLUMN FOCUSING FOLLOWED BY LIQUID CHROMATOGRAPHY AND UV DETECTION**

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Vitamins and carotenes represent important dietary components essential for health, because of their involvement in vital metabolic processes and the potential ability to decrease the risk for coronary heart disease, cancer and sight disorders. Therefore, their content in food commodities can be used as an index of the health-related quality of products. Established methods for analysis of vitamins include the chromatographic ones that are typically designed for classes of compounds, i.e. water- and fat-soluble vitamins, based on their different solubility properties and chemical structures, ranging from small organic acids to large conjugated complexes. The simultaneous determination of water and fat soluble vitamins, in addition to highly lipophilic compounds, such as carotenes, increases the complexity of an analytical method, including sample processing and storage, as well as the choice of proper solubilization solvents, which must be in tune with the chromatographic eluents. Moreover, the heterogeneity of food matrices and the potential degradation of these classes of compounds during the analysis make their quantitative determination even more demanding.

In this study, an improved LC method coupled to a multiple wavelength UV detection is described for the determination of B group vitamins (B1, B2, B3, B6 and B9), ascorbic acid (vitamin C), retinol (vitamin A), tocopherol (vitamin E), phyloquinone (vitamin K1), lycopene,  $\beta$ -carotene, and  $\beta$ -apo-80-carotenal, used as an internal standard. Chromatographic separations have been performed by an innovative core-shell C18 column packed with 2.6  $\mu$ m particles; flow rates and gradient elution programs have been carefully optimized for the total resolution of all the target analytes. An on-line focusing step was required for column head trapping of carotenes and fat-soluble vitamins, before the chromatographic run starting from an aqueous mobile phase, necessary for the elution of scarcely retained water-soluble vitamins. The potential of the proposed method has been confirmed by the analysis of tomatoes and fresh fruits.

## **AEROSOL PARTICULATE MATTER STUDY FOR THE CONSERVATION OF URBAN MONUMENTAL HERITAGE: THE CASES OF FLORENCE AND MILAN**

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Air pollution can cause a variety of environmental effects also on ecosystem and cultural heritage. Aerosol particulate matter (PM), together with gases, is the main responsible for atmospheric pollution and its effects. The damage induced by air pollution on immovable and movable cultural heritage is nowadays a topic of major concern in particular in highly polluted urban areas. To adopt mitigation actions aimed to reduce pollutants, the chemical characterization of aerosol particulate matter is mandatory. In the present studies two urban sites were considered for PM monitoring: the Museum of San Marco, Florence, located in an area of the city rather exposed to traffic and the Duomo of Milan. In Florence TSP (total suspended particulate matter) was collected during different campaigns while in Milan the deposited PM was collected by means of exposed filters. In both sites specimens of local lithotypes (Carrara marble for Florence and Candoglia marble for Milan) were exposed in parallel in order to study the degradation induced by pollution on the stone surfaces. The blackening and the yellowing of the surfaces have been also monitored. Inorganic ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$ ), short chain organic acids (acetate, propionate, etc.), organic and elemental carbon were quantified in both PM and surface deposits. From these data it is possible to draw some conclusion on the causes of the surface deterioration processes.



## A MULTITECHNIQUE APPROACH ON ANTONINIAN COINS FROM EGNATIA (SOUTHERN ITALY)

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We analyzed a collection of Antoninian coins coming from the archaeological site of Egnatia (Southern Italy).

Antoninianus (III cent. bC) was initially in silver, but was slowly debased to bronze. Each new coin had a lower amount of silver than the previous one, contributing to increasing inflation.

In 274 AD Aurelian took a series of measures to solve the crisis: acting on the nominal values, closing provincial mints and activating those under the direct control of the emperor. Moreover, a new coin was introduced, heavier but still lighter compared to the first Antoninian coins, and with a content of Ag – apparently- higher than those produced in the recent past.

Six pre-reform, six post-reform and one non-ascribable coins were analyzed.

We aimed to estimate devaluation, i.e. the gradual decrease in silver content in the alloy for pre-reform coins; to provide information on the actual effects of the monetary reform of Aurelian, i.e. the supposed enhance in the amount of silver in the reformed coins and to obtain knowledge on technological production.

Portable X Ray Fluorescence, Laser-Induced Breakdown Spectroscopy, Raman Spectroscopy, Optical and Electron Scanning Microscopy with Energy Dispersive Spectroscopy were used for the investigations.

The results revealed for all coins a Cu/Ag/Sn/Pb quaternary alloy, in which copper is the main alloying element. It was not observed a substantial difference in the amount of Ag in pre and post-reform coins.

The metallographic analysis of the microstructures highlighted a Cu/Ag biphasic structure in all the coins, as well as information on the techniques used to the manufacturing, implying a process of cold hammering of the dowels obtained by melting, in some cases followed by warming up.

## **PYROLYSIS-GC-MS OF MODERN INKS: THE FELT-TIP PENS USED BY LINA BO BARDI**

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Felt-tip pens have been employed for a wide range of objects, such as sketches, drawings, copies, architectural drawings and other technical designs. Unfortunately, the inks are usually very sensitive to light and chemical agents and the exact knowledge of their composition may be important to define the optimal conservation treatment and/or storage conditions. So far, few studies have been addressed to the chemical characterization of these materials and information on binders, fillers, dyes and pigments is still lacking.

Twenty felt-tip pens that were used by the Italian architect and designer Lina Bo Bardi (1914, Rome - 1992, São Paulo) in architectural drawings, currently subjected to conservation treatments, were investigated with a multi-technique approach (scanning electron microscopy, X-ray fluorescence, infrared and Raman spectroscopy, pyrolysis gas chromatography–mass spectrometry (Py-GC-MS)).

In this contribution the Py-GC-MS data are presented and the pyrolytic fragmentation of some dyes was proposed. The combination of these results with the previously obtained spectroscopic and elemental data [1] lead to the characterization of the felt-tip pen inks.

This work was performed in the framework of PRIN 2010-11 "Sustainability in cultural heritage: from diagnosis to the development of innovative systems for consolidation, cleaning and protection", code 2010329WPF, funded by MIUR.

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## **MULTIPLEXED CHEMILUMINESCENT LATERAL FLOW IMMUNOSENSOR FOR THE SIMULTANEOUS DETECTION OF OVALBUMIN AND COLLAGEN IN PAINT SAMPLES**

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The development of an accurate and user-friendly device for “point-of-use” analysis, suitable for the characterization of painting materials, is one of the most challenging objectives in the diagnostics for cultural heritage. Indeed, the prompt identification of painting materials and the diagnosis of their state of conservation are of utmost importance for addressing urgent restoration issues, selecting proper conservation strategies, and monitoring restoration activities. Biosensors are very promising analytical tools for rapid on-site detection of analytes in complex matrices. We recently described a biosensor for multiplex detection of type-B fumonisins and B1-Aflatoxin in maize flour samples based on a chemiluminescence Lateral Flow ImmunoAssay (CL-LFIA) coupled with a portable ultrasensitive CCD-based “contact” imaging device [1].

In this work, a multiplex CL-LFIA is presented, in which two competitive immunoassays are simultaneously performed on the same strip for detecting ovalbumin and collagen in artistic samples.

The assay involves a simple extraction of the analytes from paint samples, followed by their detection by a multiplex competitive immunoassay with CL detection employing ready-to-use analytical cartridges. The use of CL detection allowed accurate and objective analytes quantification, rather than qualitative or semi-quantitative information usually obtained employing conventional LFIAs based on colloidal gold labelling. Preliminary evaluation of the approach were performed on fresh and artificially aged paint reconstructions. By using this portable device the analysis can be performed directly where the sample is obtained (point of need) by conservator or restorers to obtain prompt information during restoration actions, thus reducing time and costs of the analysis.

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## FURTHER STEPS TOWARDS THE CHARACTERIZATION OF THE ANCIENT *FOLIUM* DYE

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The *folium* dye, extracted from *Chrozophora tinctoria* (L.) A. Juss., has been cited many times in ancient treatises for its use in painting art. Therefore its use might be common, with main concern to miniature painting. Despite this, its identification in artworks is inexplicably rare [1,2], most probably for a lack of diagnostic information. A recent work attempted to contribute to its analytical characterisation [3] and its presence has been evidenced in some instances on Western European manuscripts, but what is still missing is the comprehension of the chemical nature of the dye.

In this study we have employed various analytical techniques in order to gain structural information on *folium*. Experiments have been carried out to verify whether the information emerging from ancient treatises were reliable or not. The characterisation procedure started with an extraction step in water at room temperature and revealed that *folium* has apparently an *amphiphilic* nature, with polar moiety attached to nonpolar aliphatic or, most probably aromatic structures bearing the colour. A purification step on a C18 resin allowed the removal of the uncoloured hydrophilic compounds and the separation of a yellow and an orange fraction, both rich in flavonoids, but also of some fractions with various purple shades. These were subjected to pectolytic enzyme hydrolysis to remove the hydrophilic part of the molecule, which is made of oligosaccharides according to NMR analysis. Further on, the solution was extracted in methoxybenzene from which it emerged a purple residue that can be safely considered as the hydrophobic part of the molecule. Works are in progress with HPLC-MS, SERS-Raman, MALDI-ToF-MS, and NMR in order to finally define the structure of the dye.

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**DISCLOSING THE TECHNOLOGIES OF THE QING DYNASTY PAINTERS IN CIVIL BUILDINGS: THE MURAL PAINTINGS IN THE FIVE NORTHERN PROVINCES' ASSEMBLY HALL (ZIYANG, CHINA)**

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The *Beiwusheng huiguan* ("Meeting hall of the Five Northern Dynasties") is a complex built under the Qing dynasty (AD 1636-1912) and located in Wafangdian, near Ziyang, Shaanxi (China). The building is richly decorated by wall paintings realized in AD 1848. The paintings, including two scenes of the 'Romance of the Three Kingdoms' are a rare example of well preserved and not yet restored wall paintings of high artistic value in this kind of buildings. This paper presents the results obtained from the identification and localization of the organic materials used as binding media and colorants in the wall paintings of the main hall of *Beiwusheng huiguan*.

The chemical characterization of the paint binders was performed through a multi analytical approach consisting in the combined use of chromatographic-mass spectrometric or spectrophotometric techniques (GC/MS, Py/GC/MS, LC/MS/MS and HPLC-DAD). Proteinaceous and saccharide materials and a siccative oil were used on different paint layers [1,2]. Moreover, we assessed the use of several organic materials as colorants and lakes such as indigo and tannins. The distribution of the organic materials identified was achieved by means of Synchrotron radiation Fourier transform infrared spectroscopy [3]. Novel sample preparation strategies were used in order to obtain high quality sample stratigraphies [4]. Experiments were performed at the European Synchrotron Radiation Facility (ESRF) at the beamline ID 21.

The results obtained from the multi-analytical approach allow determining the organic materials used by the Chinese artisans, highlighting the high technique level achieved in the 19<sup>th</sup> century. The binding media and the organic colorants identified as well as their distribution allowed discussion of the painting technique

used by the painters of the Qing dynasty giving information for the first time on the decoration of civil buildings.

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## **BEEKEEPING IN IRON AGE NORTHERN ITALY, A MULTI ANALYTICAL INVESTIGATION ON HONEYCOMB REMAINS FROM THE FORCELLO ETRUSCAN SITE**

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In ancient and historical times, beeswax and honey were raw materials of crucial interest for a variety of activities from handcrafting to nutritional purposes. Rich iconographic and literary evidence of beekeeping exist, while archaeological data are strongly underrepresented. An excavation campaign in the Etruscan Forcello settlement (540 -495 BC Bagnolo San Vito, Mantua province, Italy) led to the discovery of a craftsman workshop with residues interpreted as honeycombs, bee-breads (pellets of pollen packed by honeybees and used as protein source for larvae) and *Apis mellifera* bodies, in connection with containers made in *Abies alba* wood and embedded in lumps of a dark solid material. These materials were charred during a fire involving the settlement in the 510-495 B.C.E. A multi analytical investigation was carried out on these materials in order to confirm their origin. We compared the results with those achieved by analyzing fresh and charred reference beeswax. An heating experiment was also set up on fresh bee breads from a modern honeycomb to check morphological and color variations in pollen grains under increasing temperatures, to be compared with fossil evidence from the Forcello site. Thanks to infrared spectroscopy we were able to primarily distinguish proteinaceous residues from waxes and tar, and to reconstruct the formation of the dark solid material recovered in the site. Advanced mass spectrometric techniques such as GCMS, APCI/MS and LC-ESI-QToF were employed to identify the known beeswax biomarkers such as wax monoesters, odd numbered *n*-alkanes, long chain fatty acid and alcohols. Analysis of bee breads is in progress and will provide data on honeybees floral preferences and feeding behavior.

The investigation provided useful information about the practice of production and the storing of the beeswax in the site.

## **NEW INSIGHT ON THE DEVELOPMENT OF AN ENHANCED SENSITIVITY FITR APPROACH FOR THE ANALYSES OF COLORANTS**

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In this paper we present a new enhanced sensitivity FTIR technique which allows analysis of thin layers by ATR spectroscopy. From simulations and experimental results we found that, when a film is some hundreds of nanometers thick and is applied to a metal support, an enhancement of the signal is observed with respect to normal ATR or transfectance. The angle of incidence should be just above the critical angle for the internal reflection for the element-sample interface. We named this approach the Metal Underlayer ATR spectroscopy (MU-ATR) to distinguish it from SEIRA (Surface Enhanced Infrared Absorption Spectroscopy), which makes use of metal islands in contact with the sample and SuGARS (Super Grazing Angle Reflection Absorption Spectroscopy), in which grazing conditions are employed. MU-ATR can find applications in several important fields where low or trace amounts of sample are routinely collected and analyzed. The forensic science and conservation science are just two examples. To this aim applications of this method for the analyses of dyed fibers are reported.

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## **DEVELOPMENT OF AN ELECTROCHEMICAL IMMUNOSENSOR FOR THE IDENTIFICATION OF EGG TEMPERA**

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Analysis of the materials that constitute a piece of art is an important step not only for restoration, but also for conservation purposes. To this aim, the development of an electrochemical immunosensor based on gold nanoelectrodes ensembles (NEEs) is presented. In order to identify egg-tempera, which is one of the most common painting technique used since the Thirteenth<sup>th</sup> century, we focus the attention on the glycoprotein immunoglobulin IgY. IgY is present in egg-yolk at a concentration of 5-10 mg/mL and for this particular reason it represents a reliable marker to identify egg tempera from hen's egg yolk.

Gold nanoelectrodes ensembles are prepared by electroless deposition of gold using a track-etched polycarbonate (PC) membrane as a template [1]. The polycarbonate part is affine to proteins, so that it is possible to promote the immobilization of the biorecognition element on the PC insulating surface of the NEE [2]. Moreover, NEEs present geometrical and diffusion characteristics that permit to achieve a very low detection limit; this guarantees and preserves the typical high sensitivity of the immunoassays. For these reasons, NEEs are suitable to be used as transducers of electrochemical biosensors, in this particular case, an immunosensor. The analyte investigated is the antibody IgY, that is directly immobilized on the PC; the secondary antibody used is labeled with the enzyme horseradish peroxidase (HRP). In the presence of its substrate (hydrogen peroxide) and a redox mediator (methylene blue), HRP generates an electrocatalytic signal that is proportional to the analyte concentration [3].

In this work, we focus the attention on the improvement and optimization of the analytical procedure, in order to decrease the amount of sample, which, for artwork analysis, is a critical parameter.

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## **A FIRST INSIGHT AGAINST THE FALSIFICATION OF CLASSIC CARS: CHARACTERISATION OF STEEL FROM ALFA ROMEO MUSEUM VEHICLES**

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As the classic car auction market has seen a stunning growth in values over the past decade. The trade in fake vehicles it is becoming more significant. Identifying a fake classic car is extremely difficult due to the exactitude and talent of the counterfeiters that manufacture these objects. At present, the best practice in authentication is an accurate survey of the car made by an experienced specialist with knowledge of the particular model, with inspections of the serial numbers. The use of chemical testing of the alloys or metals has been reported in non-scientific articles. The aim of this research, in collaboration with the Alfa Romeo Museum of Arese, is a first attempt at developing an analytical method able to discriminate between fake and original historic cars, through the investigation of the alloyed steel used in the chassis. Drastic technical changes occurred in the steel industry over the last 100 years, and one of the results has been an approximately constant reduction in the level of impurities (Hydrogen, Nitrogen, Oxygen, Sulphur, Phosphorus, Copper, Tin and Lead) in the alloy [1]. Steel samples and certified reference materials have been analysed with a handheld portable XRF, ICP-MS and C-S instrumentations for the purpose of validation and developing a successful and non-destructive analysis protocol for the use of handheld portable XRF in classic vehicle workshops. Having developed the analytical protocol, cars with different ages (the majority of which were Alfa Romeo) have been chosen and investigated. All the data acquired was processed using multivariate statistical techniques such as Principal Component and Cluster Analysis.

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**CHEMICAL ANALYSIS OF OPTICALLY DEGRADED DOCUMENTS OF THE TRIESTE CADASTRAL SYSTEM (1893): A SURPRISING IRON GALL INK PROTECTIVE ACTION**

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This study aims to identify causes and processes of an undesired age-related optical phenomenon in which two kind of paper – a white paper and a green one – and an iron gall ink are involved together with unavoidable environmental agents. Documents under examination are dated 1893 and come from the Trieste cadastral system archive. The green paper (lignin-containing) is a pre-printed payment order used in accounting operations and it is adjacent to a white paper (lignin-free). Diffused brown stains appear in the white paper being remained strictly and long in contact with the green one handwritten by an iron-gall ink. Micro-XRF (micro-X Ray Fluorescence spectroscopy) and ATR FT-IR (Attenuated total reflectance Fourier transform infrared spectroscopy) techniques were used to achieve information on both diagnostic organic and inorganic components. The green page induces severe yellowing on the contact side of the white, except for inked areas. Manuscript black lines of the lignin-containing page seem to protect the adjacent surface, where a mirror image appears. A particular type of mirror effect, that we propose to call “Negative Mirror Effect” (NME), is clearly evidenced. We can hypothesize the migration of oxidized brown low molecular weight extra-cellulose compounds from green recto to white verso pages. Browning process is only hindered in sharp correspondence with the areas of the green recto folio written with the iron gall ink. It acts as a physical barrier to the migration or, as second hypothesis, it is able to withhold the mobile organic compounds by way of a specific, but still unknown, interaction. In the field of scientific research on metal-gall ink corrosion, this is a really interesting and surprising case of the reverse, in which the ink itself is not the cause of the corrosion, but the unforeseen preventive agent.

## MULTIVARIATE RESOLUTION OF CARBONACEOUS RAMAN BROAD BANDS: A NOVEL APPROACH

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On March 15<sup>th</sup>, 2014 the city of Lille, following a series of particular weather conditions, was caught in a cloud of pollution. This event attracted the interest of the media and the scientific community who, immediately, carried out ambient air samplings in order to collect the particulate matter contained therein.

Atmospheric aerosols are complex mixtures of natural and anthropogenic particles suspended in the air. With sizes ranging from a few nanometers to tens of micrometers and atmospheric residence times as long as several weeks, aerosols can affect the air quality as well as the global climate.

Chemical characterization of individual particles at the micrometer scale is a challenging task. With this purpose, confocal Raman micro-spectrometry, which combines the spatial resolution of optical microscopy and the molecular analysis capabilities of Raman scattering, was used. In particular, the attention was focalized to core-shell carbonaceous particles.

It is well documented, by means of curve fitting techniques, that carbonaceous materials present two broad bands in the spectral region 1000-1800  $\text{cm}^{-1}$ , corresponding to the combination of five unresolved bands called D1, D2, D3, D4, and G [1,2].

The aim of this work is to extract simultaneously, from the Raman spectral images, all spectra of pure species and their corresponding spatial distribution within the micrometer scale, by using the multivariate curve resolution (MCR) technique [3].

To the best of our knowledge, it is the first time that this multivariate technique is applied to this problem.

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## AUTHENTICATION OF *BOLETUS EDULIS* AND ALLIED SPECIES BY NEAR INFRARED SPECTROSCOPY AND CHEMOMETRICS

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Out of all the wild mushrooms in the world, there are few as prized and sought after as *Boletus edulis* and allied species [1]. These macrofungi, known as “porcini mushrooms”, represent almost totality of mushrooms placed on the market, both fresh and dehydrated.

Nowadays few boletes on the Italian market have Italian origin: in most cases, they are collected in Eastern Europe and China, dried on site, and then, after a first selection, imported into Italy. It is not rare to find, among such imported dried boletes, mushrooms to different – less valuable – species. Analyses performed to define macrofungi eligible for sale are mainly based on naked eye inspection by mycologists, aimed at identifying alien species and/or macromorphologic alterations.

The species that are most commonly used for adulterating boletus mushrooms is *Tylopilus felleus*. It is morphologically very similar to *B. edulis*, but very different from an organoleptic point of view. So, *Boletus edulis* and *Tylopilus felleus* can be confused with each other by visual inspections, but a taste test would allow to differentiate them, since *B. edulis* is savory while *T. felleus* is intensely bitter. *Boletus edulis* derived products may be adulterated even with the purplish-hued Asian species *Boletus violaceofuscus*. It is quite distinct in appearance, presenting a dark violet color and a conspicuous white reticulation on the stipe [2]. Anyway, identification of small amounts of such a species within dried specimens could be not so straightforward.

Up to now, no instrumental analytical methods have been proposed for authentication of dried *Boletus edulis*. These species are currently distinguished only by visual inspections performed by mycologists on the carpophores or by microscopic examination of spores.

This study presents, for the first time, a method based on near infrared spectroscopy (NIRS) coupled with chemometrics to detect the fraudulent addition of other mushroom species in *Boletus edulis* products.

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## ANCIENT STAMPS: REGUMMED OR NOT? A PATTERN RECOGNITION-SPECTROSCOPIC STUDY

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Since the beginning of postage stamp production, counterfeiters started their activities by altering genuine stamps in some way to make them more desirable. These activities include the application of new gum on the back side of non-cancelled stamps, whose condition greatly influences the stamp value. If a stamp is identified as “regummed” by a philatelic expert, it is downgraded and considered as a stamp without gum, considerably decreasing its value [1,2]. Because these counterfeits are not always easily detected by philatelic expert visual inspection, a reliable scientific detection method is desirable. It is well documented that the three main glues used in Italian stamps during the period investigated were animal glue (before 1901), Arabic gum (1901-1973), and polyvinyl acetate glue (PVAc) (after 1974) [3]. It has also been reported that many counterfeits have been performed in recent years by applications of modern synthetic glues, such as PVAc, on ancient stamps [3,4].

The aim of this work was to study and to develop, for the first time, a rapid and non-destructive methodology able to study the stamp gum composition and to unmask regummed stamps by means of FT-NIR and FT-Raman spectroscopies.

A total number of 113 non-cancelled Italian stamps, covering the period 1861-2001 were analysed and eight ancient specimens (period 1862-1932) were purposely regummed with a PVAc thin layer, to simulate counterfeit and used as test samples.

The results obtained indicate that both of the spectroscopic techniques, coupled with exploratory pattern recognition methods, are able to detect the compositional chemical differences between the different gum and are able to detect ancient stamps artificially regummed with PVAc glue.

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**BEER FINGERPRINTING AND MULTIVARIATE DATA ANALYSIS TOWARDS INFORMED TAILORED FOOD CONSUMPTION.**

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There is increasing awareness of consumer and society in general towards all aspects, which concern food consumption encompassing ethics, sustainability, health, safety, quality, tradition, communication, marketing, etc. Research in food chemistry area has mainly focused on chemical analysis and characterization to contribute to fundamental issues such as food safety and quality, nutritional and health requirements. Aim of this work is to go a step beyond that. Could our analytical chemistry expertise be of use and ease in the cultural and gastronomic aspect linked to food consumption? In particular, could we think of developing new tools to aid consumers when choosing foodstuff to have proper knowledge of it, and producers to meet consumer expectations while using food quality as drivers?

To this aim our proposal is to use analytical spectroscopy to capture salient features of foodstuff (fingerprint) and build a reference database that can be efficiently searched through multivariate data analysis tools and linked to apps for mobile smart devices implemented for consumers inquires. At the same time consumer choice may be oriented by showing how products of similar categories cluster according to different criteria.

As a first benchmark to develop these ideas we present a survey on beer. Beer is one of the most consumed alcoholic beverages with a highly relevant economic impact associated. However, our interest is mainly due to the fact that recently the consumers favor more and more artisanal product coming from local brewery and micro- brewery weighting much more the cultural and quality aspects linked to its consumption. This may be a very positive trend in order to prevent alcoholic disorders especially in young.

Several beer samples differing by e.g. yeast, brewtype, brewery, have been collected and NIR, NMR, GCMS fingerprinting together with sensory attribute and merceological parameters have been acquired. Multivariate explorative and clustering tools are employed to group beer according to several search criteria.

## FROM HYPERSPECTRAL IMAGES TO SIGNALS: COMPARISON OF DIFFERENT DATA REDUCTION METHODS FOR FAST EXPLORATION AND CLASSIFICATION OF GREEN COFFEE SAMPLES

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Coffee varietal differentiation based on NIR spectroscopy has been widely investigated in the last 20 years. In this work, we have applied hyperspectral imaging in the NIR range (900-1700 nm) for the classification of green coffee samples into *Arabica* and *Robusta* varieties.

Twelve repeated images were acquired on each one of the 31 green coffee samples delivered in 4 different days. Each resulting hyperspectral image was converted into three kinds of signals: 1) average spectrum (AS, 150 points long signal), 2) single space hyperspectrogram (SSH, 1200 points long signals) and 3) common space hyperspectrogram (CSH, 1050 points long signals). The hyperspectrograms<sup>1</sup> are built by compressing the useful information contained in each hyperspectral image into a signal composed by the frequency distribution curves of quantities calculated by PCA (scores, Q residuals, Hotelling T<sup>2</sup>); a single PCA model for each image is used for SSH, while CSH is based on a common PCA model for all the images. This procedure allows to compress the information conveyed by the hyperspectral images, maintaining at the same time both spatial- and spectral-related features.

PLS-DA was used as classification method firstly on single AS, SSH and CSH datasets of signals, then on fused data. Data fusion was performed both at the low level, i.e., by simply merging the datasets, and at the mid level, i.e., by merging the first 20 PC scores obtained by applying PCA to each single dataset of signals. For validation purposes, the samples were split into a training set including the data collected during the first two days of analysis and into two test sets (corresponding to day-3 and day-4 deliveries) to mimic controls on incoming batches in the industrial plant.

All the classification models show good prediction results for day-3, while for day-4 all the models except those obtained on AS data gave lower efficiency values. A more detailed investigation revealed the occurrence of an instrumental fault on day 4 (due to the detector cooling system), that caused striping in the images. Average spectra gave models less prone to instrumental variability; on the other hand, hyperspectrograms may be used to check the stability of the imaging system.

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**TRACEABILITY STUDY OF HAZELNUTS ALONG THE CHAIN OF PRODUCTION OF HAZELNUT PASTE IN A CONFECTIONERY BY THE DETERMINATION OF THE ELEMENTAL PROFILE BY ICP-MS AND MULTIVARIATE STATISTICAL METHODS**

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It is certainly of great interest in confectionery the availability of tools for the traceability of the origin of hazelnuts along the production chain of the hazelnut paste, in order to identify possible frauds. Hazelnuts from different origins (both within the Italian territory and from abroad) in fact show a quite wide range of organoleptic features reflecting in a quite different commercial value of the raw material. While the cultivar of hazelnuts can be quite easily identified by a direct visual inspection of the raw entire hazelnut by its morphological characteristics, it is usually impossible to distinguish different cultivars when they are sold already chopped.

The elemental profile, which proved to be related to the origin of different products, was therefore determined for hazelnuts of different Italian origin (corresponding to different cultivars) along the chain of production of the hazelnut paste (i.e. along the chain: raw and roasted hazelnuts and their paste) by ICP-MS and ICP-OES after microwave digestion. The data were then treated by multivariate statistical tools, as Principal Component Analysis and Classification methods. The elemental profile proved to be a good choice for the evaluation of the traceability of the raw material along the chain of production.

## **COUPLING OF NIR SPECTROSCOPY AND CHEMOMETRICS FOR THE AUTHENTICATION OF DRIED FRUITS**

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Dried fruits are complex matrices, rich in nutrients, fatty acids and other bioactive compounds, so that, by virtue of their particular composition, in recent years the attention paid to the possible benefits associated with consumption of these products has significantly increased. Accordingly, the number of people who consume dried fruits of various nature, not only for their characteristics hedonic-organoleptic, but also for dietary or health reasons is constantly growing. Consequently, on the basis of consumer demand and to strengthen the economic competitiveness of the products (in particular of almonds and hazelnuts), the European Union, which is one of the leading producers and consumers of almonds and hazelnuts, has put in place strategies to enhance the quality and characteristics linked to geographical origin of some dried fruits, through the awarding of PGI and PDO marks for specific products.

In this framework, it is clear that there is the need to develop an analytical approach that allows authentication and traceability of products of designated origin, to protect producers, traders and consumers from possible frauds that may occur when the product in question is partially or totally replaced with dried fruit of inferior quality.

Based on these considerations, the present study addresses the possibility of developing an integrated analytical approach for the geographical traceability of samples of almonds or hazelnuts.

For this purpose, samples collected from different sources were characterized by near infrared spectroscopy and the recorded signals represented the experimental basis for the development of classification models, built using both a discriminant (PLS-DA) and a modeling (SIMCA) approach.

From an experimental standpoint, NIR spectroscopy was chosen as it allows a rapid, robust, efficient, sensitive, and cost-effective determination, also since it does not require any kind of sample preparation and goes in the direction of green analytical chemistry.

**N3 AND BNN: TWO NEW SIMILARITY BASED CLASSIFICATION METHODS IN COMPARISON WITH OTHER CLASSIFIERS**

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Two novel classification methods, called N3 (N-Nearest Neighbours) and BNN (Binned Nearest Neighbours), are proposed. Both methods are inspired to the principles of the K-Nearest Neighbours (KNN) method, being both based on object pairwise similarities.

Their performance was evaluated in comparison with eight well-known classification methods. In order to obtain reliable statistics, several comparisons were performed using 32 different literature data sets, which differ for number of objects, variables and classes.

Results highlighted that N3 on average behaves as the most efficient classification method with similar performance to support vector machine based on radial basis function kernel (SVM/RBF). The method BNN showed on average slightly higher performance than the classical K-Nearest Neighbours method.

## **WEIGHTED REGULARIZED HASSE FOR CRITERIA WEIGHTING AND INCOMPARABILITY REDUCTION**

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This work presents a modified version of Hasse Diagram (HD) technique, the weighted Regularized Hasse. HDs are useful for Multi-Criteria Decision (MCD) issues, since they define a partial order between different alternatives based on their variable values; however, they are characterized by a large number of incomparable objects when many criteria are present.

Weighted Regularized Hasse technique aims firstly to reduce the number of incomparabilities, by a simple mathematical threshold acting on the definition of incomparability. Moreover, this technique also allows to: (1) weight criteria according to their relevance, thus allowing for a more rational application; (2) acquire statistics about the family of the obtained (weighted regularized) Hasse matrices and the consequent partial orders.

In this work, Weighted Regularized Hasse Technique was tested on several MCD datasets taken from literature, showing how: (1) the number of incomparable objects can be successfully reduced, and (2) the weights can be used to tune criteria contribution to the final outcome. Moreover, by varying the mathematical threshold, one can obtain statistics that reflect the relevance of the ordering of each object, also gaining information on data structure.

## **IDENTIFICATION OF SULFORHODAMINE B PHOTO-DEGRADATION PRODUCTS PRESENT IN NON-PERMANENT TATTOOS BY MICRO LC-QTOF MS/MS**

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Tattooing is an ancient form of art, first employed in prehistory, spread in every part of the world. It has become more and more popular in recent years. The reasons for being tattooed are different and concern group or tribal affiliation, social identification and personal artistic expression. In the literature there are many studies about permanent ink toxicity, but they mainly deal with metal allergies (nickel, lead and cadmium). On the contrary, this study considers the sulforhodamine B, also called Acid Red 52, a permitted dye largely used in non-permanent tattoos, a type of body decoration widespread in children. It is possible, as a matter of fact, that non-toxic allowed dyes may originate toxic species after exposure to sunlight irradiation. Degradation evidences were obtained from both aqueous and sweat-simulating solutions of the dye after 9 days of solar box irradiation.

The identification of the degradation products was achieved by using a non-target approach. For this purpose, a new micro liquid chromatography method coupled to tandem high-resolution mass spectrometry was developed. The method was validated evaluating LOD, LOQ, linearity range and intra- and inter-day precision. The identification of the degradation products was carried out by using a multivariate approach, mainly based on Principal Component Analysis and Discriminant Analysis. Five degradation products and two impurities of the dye were identified and their chemical structures elucidated. The degradation products were the same for both types of solutions, whereas the degradation rate of the dye in sweat-simulating solution ( $t_{1/2} = 1.6$  days) was slightly faster compared to the one observed in aqueous solution ( $t_{1/2} = 1.9$  days).

In order to better simulate the irradiation effects on the dye used on the skin, the method was also applied to samples of tattooed pigskin subjected to irradiation. None of the degradation products found in the sulforhodamine B solutions could be identified in the degraded tattooed pigskin samples, but a new signal at  $m/z$  637.3051 (positive ionization) was found and the structure of the corresponding molecule was elucidated [1]. The mutagenicity of the photo-degradation products was evaluated using a QSAR approach, which gave negative results for all the structures elucidated.

[1] F. Gosetti, B. Bolfi, E. Marengo, *Anal. Bioanal. Chem.*, in press DOI: 10.1007/s00216-015-8667-5

## MAJOR SOYASAPONINS IN TRADITIONAL CULTIVARS OF FAGIOLI DI SARCONI BEANS INVESTIGATED BY LIQUID CHROMATOGRAPHY AND HIGH-RESOLUTION TANDEM MASS SPECTROMETRY

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Soyasaponins are secondary plant metabolites containing sugar chains linked to triterpenes [1]. Recent work has revealed that soyasaponins in leguminous plants might have health benefits, including the prevention and treatment of diseases, so called nutraceutical properties [2]. Common bean (*Phaseolus vulgaris* L.) is one of the most important legumes, widely cultivated due to its commercial value and its high content of nutrients such as carbohydrates, proteins, minerals, and vitamins. The current study investigates for the first time the major soyasaponins occurring in Fagioli di Sarconi beans (ecotype Tabacchino). The analytical approach is based on the separation/detection by reversed-phase liquid chromatography (RPLC) coupled with positive electrospray ionization (ESI) and infrared multiphoton dissociation (IRMPD) in high-resolution FTICR-MS. The high mass accuracy allowed to identify unequivocally the main group B soyasaponins, namely soyasaponin I (Soy I), soyasaponin V (Soy V), soyasaponin  $\beta$ g (Soy  $\beta$ g) and soyasaponin  $\alpha$ g (Soy  $\alpha$ g). Protonated adducts of soyasaponins I, V,  $\beta$ g and  $\alpha$ g were observed at  $m/z$  943.5262, 959.5213, 1069.5583 and 1085.5534, respectively. Both soyasaponins  $\beta$ g and  $\alpha$ g are conjugated forms at the C-22 position with the 2,3-dihydro-2,5-dihydroxy-6-methyl-4H-pyran-4-one (DDMP) moiety, which is well recognized as a scavenger of reactive oxygen species. The occurrence of this product ion at  $m/z$  127.0389 ( $[\text{C}_6\text{H}_6\text{O}_3+\text{H}]^+$ , DDMP) was successfully evidenced by IRMPD FTICR-MS experiments [5].

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**THE ENTIRE SUITE OF CARDIOLIPINS IN A BACTERIAL EXTRACT EXAMINED BY REVERSED-PHASE LIQUID CHROMATOGRAPHY WITH ELECTROSPRAY IONIZATION AND MULTISTAGE MASS SPECTROMETRY**

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Cardiolipins (CLs) are minor components of bacterial and mitochondrial membranes. In bacteria, CLs interact with energy metabolism proteins, respiratory complex, and is assembled into reaction centers, and is also involved in proper localization of proteins on membrane [1]. Bacterial membranes contain low steady-state levels of CLs, which increase only during the stationary growth phase and under certain conditions of environmental stress [2]. The mechanism by which CLs stabilize bacterial membranes is not known and their structural characterization, along with a quantitative analysis, could provide useful information on this topic.

In this communication the characterization of CLs occurring in the carotenoid less *Rhodobacter sphaeroides* R26 grown photosynthetically, performed by liquid chromatography (LC) coupled with electrospray ionization (ESI) and multistage mass spectrometry (ESI-MS<sup>n</sup>, with n = 2,3), is described. A reversed phase fused-core C18-amide column and a gradient elution with water/methanol both containing 2.5 mM ammonium acetate was employed. Along with the already known [3,4] 70:4, 70:3 and 72:4 CLs ([M-H]<sup>-</sup> ion at *m/z* 1428.0, 1430.0, 1456.0 respectively) [4], several, previously unrecognised, isobar/isomer CLs were found to occur in *R. sphaeroides*. In detail, the identification of the 64:3, 64:2, 64:1, 66:3, 66:2, 66:1, 68:2, 70:2, 72:3 and 72:2 CLs was achieved for the first time. Interestingly, the occurrence of three chromatographically separated 72:4 isomeric CLs corresponding to (18:1)<sub>4</sub>-CL was demonstrated, thus suggesting the occurrence of at least two 18:1 acyl chains, most likely vaccenic (which is the most abundant in *R. sphaeroides*) and oleic differing in the double bond position, i.e., Δ<sup>11</sup> and Δ<sup>9</sup>, respectively.

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## **SILICON AND METAL-SILICON NANOWIRE ARRAYS FOR LASER DESORPTION IONIZATION MASS SPECTROMETRY APPLICATIONS**

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Since its introduction in '80s, matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) has been extensively used in the analysis of large biomolecules such as proteins, nucleic acids, and synthetic polymers. Nevertheless, applications of this technique in the low molecular weight (LMW) region (below 700  $m/z$ ) were limited due to the spectral interferences derived from the commonly employed organic matrices. Moreover, inhomogeneous crystallization often contributed to poor ionization reproducibility. In this light, many efforts have been made to propose efficient alternatives, as for instance, the use of inorganic matrices.

In particular, nanomaterials can overcome these problems since they exhibited low background interference and facilitated homogeneous sample deposition thus improving shot-to-shot reproducibility [1-3].

Here, silicon nanowire arrays (Si NWs), prepared by a maskless wet-etching technique, assisted by the deposition of an ultrathin gold film on a Si substrate [4], are successfully applied as DI promoters for the LDI-MS analysis of different LMW analytes. Alternative metal nanoparticle-SiNWs are deposited, as well. The method is in general very fast since it is performed simply depositing the analyte solutions onto a modified MALDI target. Different NW lengths and compositions have been tested, and the relevant data have been combined with surface spectroscopy and morphological characterizations, providing a correlation between the nanomaterial properties and MS performance level.

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## **SIMULTANEOUS DETERMINATION OF HALOGENATED CONTAMINANTS (PCBs AND PCNs) AND POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN BIOTA INTEGRATED INTO A SINGLE METHOD**

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In this study, a novel analytical approach for the simultaneous determination of 127 polychlorinated biphenyls (PCBs), together with 6 polychlorinated naphthalenes (PCNs) and 16 polycyclic aromatic hydrocarbons (PAHs) was developed and validated.

The number of environmental contaminants which undergo legislation continues to increase, fostering the development and validation of sensitive, selective, fast and inexpensive analytical methods.

The determination of such analytes often requires long and expensive procedures for each class of compounds. This does not allow the rapid and fast analysis of large quantity of samples for food safety screening purposes.

The aim of this study was to develop a method for the simultaneous determination of PCBs, PCNs and PAHs in biological samples (bivalves tissues) from extraction to instrumental analysis.

The method uses pressurized liquid extraction (PLE), gel permeation chromatography (GPC) for lipid fraction removal, automatic preparative liquid chromatography for the clean-up and a single run in HRGC-LRMS.

We integrate analyses of these three groups of POPs into a single analytical protocol from sampling to injection. Not only does this method a lower amount of sample and less time, but it also allows one to increase the sample throughput.

The use of one single pre-analytical method allows one to simplify the procedures and save time, while the single run in GC-MS enables the collection of more data simultaneously and in less time (about 75 minutes for 149 analytes) compared to separate analyses.

## **A NEW APPROACH TO DETECT ANTIBIOTIC RESIDUES IN MUSCLE TISSUES: DEVELOPMENT OF A HIGH RESOLUTION MASS SPECTROMETRY SCREENING METHOD**

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A very common practice to screen antibiotic residues in sample of animal origin is based on microbiological assays using plate test bacterial growth inhibition techniques. These methods are able to cover many antibiotic classes, offering low-cost analysis. However, due to their detection mode microbiological assays do not permit to discriminate one antibiotic from another one and, for several compounds, do not reach the maximum residue limits (MRLs) set by European Commission regulation (EU) 37/2010/EC [1]. Due to these drawbacks, we developed a LC-HRMS procedure for the screening of more than 70 antimicrobial compounds belonging to the following veterinary drugs families: amphenicols, beta-lactams, diamino-pyrimidine, lincosamides, macrolides, pleuromutilins, quinolones, rifamycins, sulphonamides and tetracyclines.

To be able to analyze at the same time all these compounds with different physical and chemical properties, generic and non-selective sample preparation procedure has been optimized. Muscle samples were extracted twice: at first with a acetonitrile/water mixture and then with acetonitrile. The extract was evaporated to dryness and the residue was dissolved in ammonium acetate buffer. Mass spectrometric determination was carried out on LTQ-Orbitrap mass spectrometer XL operating in full scan acquisition mode at a resolving power of 60.000 full width at half maximum (FWHM). The high resolving power combined with high mass accuracy (< 5 ppm) allow to detect a specific analyte of interest just knowing the exact mass of the molecular ion and the corresponding LC retention time.

The proposed method has been successfully validated demonstrating a detection capability (CC $\beta$ ) equal to 10  $\mu\text{g kg}^{-1}$  for all the investigated compounds [2]. Therefore it is applicable to routine official control of antibiotic residues in muscle samples replacing the traditional screening test currently used in Italy.

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**ULTRA HIGH PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED TO HIGH RESOLUTION TANDEM MASS SPECTROMETRY: ACQUISITION STRATEGIES TO CHARACTERIZE COMPLEX PHYTOCHEMICAL MIXTURES. APPLICATION TO STRAWBERRY EXTRACT**

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Nowadays, with the advent of the last generation instrumentation, high resolution mass spectrometry (HR-MS) has become available to many operators. HR-MS allows to obtain the accurate masses of even unknown compounds, providing a valuable tool for their molecular formula identification; however, structural information can only be obtained if HR-MS/MS experiments are performed too. The newest HR mass analyzer introduced into the market is based on Orbitrap technology. Different stand-alone or hybrid instruments based on this mass analyzer are available, however, when the goal is the identification of unknown compounds in complex mixtures, configurations able to provide both HR-MS and HR-MS/MS spectra at high scan speed are needed. This requirement is particularly important when the mass spectrometer is preceded by a chromatographic system able to provide separation of tens of compounds in few minutes, such as an ultra high performance liquid chromatography (UHPLC) system.

In this work, UHPLC coupled via electrospray (ESI) source to a hybrid quadrupole-Orbitrap mass spectrometer was employed to analyze a complex phytochemical mixture; strawberry extract was chosen as sample test.

To obtain the maximum separation in a short analysis time, two core-shell (2.6  $\mu\text{m}$  particle size) C18 chromatographic columns were connected in series and operated at 600  $\mu\text{L min}^{-1}$  flow-rate.

Mass spectra were acquired in both positive and negative ESI ionization modes. Because strawberry, as most plant organs, contains flavonoids, polyphenols and other natural compounds in various conjugated forms, an acquisition method involving first a full scan, then MS/MS acquisition of those precursors showing certain neutral losses, was used. Neutral loss of the main glycoside moieties (glucose, rhamnose, pentose, and their derivatives) was set. To obtain more information, also classical data dependent MS/MS acquisition was performed.

In most cases, accurate masses of both precursors and fragments showed errors below 1 ppm. Mass spectra were analyzed and compared with the literature data and with the few mass spectra databases available, allowing the identification or the tentative identification of about 100 compounds, most of them in mono- and di- glycosylated form.

## **DETERMINATION OF KNOWN/UNKNOWN IODINATED POLLUTANTS IN AQUATIC ECOSYSTEMS USING FULL-SCAN TANDEM MASS SPECTROMETRY TECHNIQUES**

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The analysis of emerging contaminants in natural water sources is based primarily on the analysis of “known-unknowns”. These are compounds whose identities are known and several of their chemical or physical properties are tabulated in a database. Here we present an analytical strategy for the determination of pollutants with unknown structures based on liquid chromatography and full scan tandem mass spectrometry with detection based on structural features that suggest the potential toxicity of the unknown. This experimental strategy has been applied to the detection of iodinated X-ray contrast agents (ICM). Conventional wastewater treatment plants (WWTP) have shown to be unsuitable for a complete elimination of ICM, which have thus been found in WWTP effluents and in surface water. Once in the surface water, they could be transformed through different processes and form several transformation products, that need to be monitored as well. For such, we combined laboratory experiments with in field analyses. A sunlight simulator apparatus was used to irradiate different aqueous solution of the selected pollutants in the presence of a catalyst, aimed to generate photoinduced transformation products similar to those occurring in the environment. Analyses were performed by liquid chromatography-LTQ-FT-Orbitrap mass spectrometry. Unknown compound were characterized by analyzing MS and MS<sup>n</sup> spectra, whereas HRMS with MS/MS fragmentation was used as a confirmatory step for proper identification of compounds in natural water.

Furthermore, we used precursor ion scanning for 127 *m/z* ion that is specific for iodine-containing compounds. Precursor ion scanning for iodine ions is carried out over consecutive, narrow mass ranges using several injections. The identification of unknown compounds is facilitated by accurate mass and product ion determinations of the iodinated compounds detected during precursor ion analyses. Ultimately, the unknown iodinated compounds are identified by comparing its spectroscopic characteristics and retention time with analytical standards suggested to have the same empirical formula as the unknown. We focused on iopamidol, iopremide and amidotrizoic acid and on their transformation products. All compounds have been searched for in several branches of the Chicago River and wastewater effluent.

## CHARACTERIZATION OF ADDUCTS BETWEEN CYCLODEXTRIN-CAPPED GOLD NANOPARTICLES AND BIOMOLECULES BY TAYLOR DISPERSION ANALYSIS AND CAPILLARY ELECTROPHORESIS

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The aim of this work has been the study of the diffusion properties of the adducts between heptakis (6-deoxy-6-thio) ciclomaltoheptatose-capped gold nanoparticles (Au/ $\beta$ -CDSH NPs) and molecules of biological interest. In particular, we focused on 2'-deoxycytidine (DC), a nucleoside whose analogues have been used as potential anticancer and/or antiviral agents and doxorubicin hydrochloride (DOXO), a drug commonly used for the treatment of a wide range of cancers. The diffusion of both individual components and their mixtures has been studied to evaluate the interactions between capped nanoparticles and biologically active molecules. This information is important to assess the use of Au/ $\beta$ -CDSH NPs as medium for the transportation and the controlled release of drugs in the development of new strategies for drug delivering [1].

Experimental measurements were carried out by capillary electrophoresis (CE) . Diffusion experiments were performed by using two injection modes, either solute pulse (where an hydrodynamic injection of the sample is followed by the application of a mobilization pressure) or solute front (where mobilization pressure is applied directly to the sample). Non-ideality of CE experiment were accounted for. Taylor dispersion theory (TDA) has been employed for data interpretation [2]. Diffusion coefficients obtained for the adduct between Au/ $\beta$ -CDSH NPs and DC have found to be in good agreement with values obtained with other techniques [3]. This shows that TDA-CE) is an effective technique for the determination of the diffusion coefficients of NPs and their adducts. Moreover, these experiments allow for the estimation of: (a) the hydrodynamic radius of NPs and their adducts; (b) the bounded fraction of biomolecules (DC and DOXO) onto NPs and (c) the formation constant of the adducts.

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## INVESTIGATING THE FEASIBILITY OF COUPLING QuEChERS EXTRACTION, ON-LINE CLEAN-UP AND LC-MS/MS ANALYSIS OF EMERGENT MICROPOLLUTANTS IN SLUDGES

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The determination of organic micropollutants of high environmental concern (e.g. carcinogenic and/or toxic and/or endocrine disrupting compounds) in sewage sludge is of great importance when this wastewater treatment by-product is recycled in land application. Furthermore, the assessment of micropollutant concentration levels in sludge is highly relevant in order to highlight actual degradation processes as well as matrix transfer phenomena within the evaluation of wastewater treatment plant (WTP) efficiency. Among the various environmentally relevant organic micropollutants, pharmaceuticals, by their nature, have a strong ability to interact with the endocrine systems of human beings and animals. The pharmaceutical compounds are widely administered to humans and animals, being then excreted as such and/or as metabolites, thus reaching WTPs and, in the presence of an incomplete removal, surface waters too [1]. Within the class of pharmaceutical compounds, nonsteroidal anti-inflammatory drugs (NSADs) are without doubts among the most utilised in Italy, as well as developed countries [2].

In this study the feasibility of the determination of 7 common NSADs and 6 hydroxylated metabolites in sewage sludge from GIDA (Prato, Italy) WTPs, by QuEChERS extraction [3] coupled with online SPE clean-up and liquid chromatographic-tandem mass spectrometric analysis, was investigated. Method development and optimization involved the selection of the stationary phase and gradient elution, followed by online SPE conditions and H<sub>2</sub>O/CH<sub>3</sub>CN ratio in the QuEChERS extraction. The overall method was investigated for apparent recovery, source-dependent matrix effect, method detection and quantification limits, using labelled analytes. The method is suitable for the determination of target analytes in the range of tens to hundreds µg/kg of dried sludge, with a total analysis time per sample less than 30 minutes.

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**EFFECT OF COSURFACTANT ON SEPARATION SELECTIVITY IN SOLVENT-MODIFIED MEKC: THE DICLOFENAC CASE**

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Solvent-modified Micellar ElectroKinetic Chromatography (MEKC) shows performances in selectivity tuning and separation efficiency similar to MicroEmulsion Electrokinetic Chromatography (MEEKC) [1], with the advantage of much greater composition flexibility of adding modifiers to the background electrolyte. In our previous study, a MEEKC method with the addition of methyl- $\beta$ -cyclodextrin was developed for the simultaneous assay of diclofenac and its impurities, involving both neutral and charged compounds as analytes. In the scouting phase for selecting a suitable operative mode, the presence of the cosurfactant *n*-butanol, both in MEEKC and in MEKC, was found to be compulsory in order to achieve the separation, demonstrating that cosurfactant plays an active role in controlling the partition and migration of the analytes. Based on these results, this study presents a comprehensive investigation on the effect of the cosurfactant on separation selectivity in SDS-based MEKC, performed by Molecular Dynamics (MD) and NMR, in order to contribute to the understanding of the involved intermolecular interactions. MD constitutes an essential tool for exploring the mechanism of molecular recognition and NMR should be used to confirm the experimental and simulation results. From the retention behavior of the solutes, information with respect to the physical and chemical properties of the analytes, such as the extent of solute association with micelles, was obtained. Capacity factors and effective mobilities of the solutes were calculated and compared with the potential and the gain energy of inclusion complexes between analytes with SDS and *n*-butanol obtained by MD. Nuclear Overhauser effect spectroscopy NMR (NOESY) experiments were carried out to confirm the mechanism of separation.

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## REDUCING THE PHTHALATES CONTAMINATION DURING THE ANALYSIS PROCESS USING GAS PURGE MICROSYPHINGE EXTRACTION.

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Phthalate esters (PAEs) are commonly used as non-reactive plasticizers in vinyl plastics to increase the flexibility of plastic polymers [1]. Numerous studies reported about the PAEs as a class of endocrine-disrupting chemicals [2]. In addition, these studies also showed that a major source of human exposure to phthalates is the diet [3]. To date, the largest problem in PAEs analysis is the contamination due to the wide and uncontrolled PAE presence in the environment, including chemicals and glassware: sample contamination may then occur in every step of the analysis process. To reduce the possibility of contamination during sample handling, it is then necessary to shorten the pretreatment step, and to keep the analysis procedure as simple as possible. Gas purge microsyringe extraction (GP-MSE) [4] is a fast technique, suitable for miniaturization, with no plastic components in the whole device that works under a nitrogen flow, and it can be considered a good candidate to reach this goal. In fact, with GP-MSE a new and low-blank-value analytical method for the analysis of PAEs in foodstuffs was set-up. The overall recoveries ranged from 85.7 to 102.6%, and the RSD was less than 10%. This method has been applied in the monitoring of PAEs in 78 foodstuffs. The results showed that a wide variety of PAE concentrations were found in the different groups, and the highest content of PAEs (in the range 658 - 1610 ng g<sup>-1</sup> fresh weight) was found in seafood. The concentration values found in food were in the following order: DEHP > DBP > DEP ≈ DMP > BBP ≈ DNOP. Finally, the daily intake of PAEs was estimated for adults based on the levels of PAEs in foodstuffs. The total estimated daily intakes of PAEs, calculated in terms of DEHP amount, ranged from 3.2 and 12.9 mg kg<sup>-1</sup> bw d<sup>-1</sup>.

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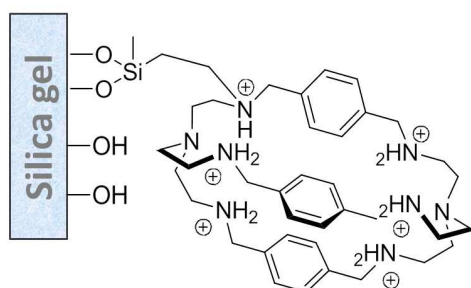
## SUPRAMOLECULAR RECEPTORS IN SOLID PHASE FOR ANIONIC RADIONUCLIDES SEPERATION

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Methods for the separation and concentration of anion species in solution are quite uncommon, with respect to metal ions, despite the importance of anions in many fields (e.g. environment, industry, biology and medicine).[1] and, in particular, selective molecular receptors for hazardous and radioactive anions are of great awareness. Our interest was towards the pertechnetate anion (i.e. stable form of technetium), especially noteworthy among radioactive pollutants, and perhenate and pertechnetate, produced in the  $^{188}\text{W}/^{188}\text{Re}$  or  $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$  generators and used in diagnostic and therapy.

The large size and low charge density of both pertechnetate and perhenate make the selective recognition and separation a great challenge.

In a previous work, we selected an azacryptand, that in the hexaprotonated form, is the most suitable for  $\text{Re}(\text{Tc})\text{O}_4^-$  encapsulation, together with the silica  $63\ \mu\text{m}$  as solid phase, particularly for the best performance with respect to other solid phase in column operation. [2-3] See figure 1.



**Fig 1** the silica modified with (3-iodopropyl) trimethoxysilane, after reaction with the azacryptand receptor.

From these findings, we oriented the present investigation to set up the operative conditions in an automated system for the production of pure Rhenium (Technetium) in a suitable medium with high activity high  $\text{Re}(\text{Tc})/\text{Mo}$  ratio, as required for medical applications in the field.

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## FLUORESCENT MESOPOROUS SILICA MATERIALS DISCRIMINATING Ag(I) AND Hg(II)

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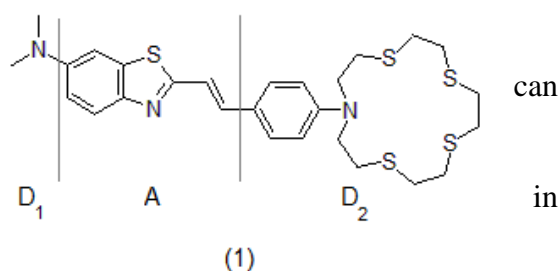
A new hybrid sensing material consisting of a fluoroionophore embedded in mesoporous silica that discriminate between Ag(I) and Hg(II) was prepared. Benzothiazole-based molecule (**1**), already studied in solution [1], is not soluble in water.

Simple steric adsorption into the

pores of suitably functionalized SBA-15 microparticles however is possible. Various functionalization strategies for the silica were tested (two different silanes grafted only onto the outer particle surface or onto the inner pore walls and outer surface) leading to four different materials. After steric loading the materials were washed with water and dried. The material functionalized with propyltriethoxysilane on the inner and outer surface (**PrpAA**) proved to be the best performer, possibly because of the non-polar environment which allows for good immobilization of the dye and strong binding of the ions.

For the analyses, **PrpAA**, suspended in water, shows fluorescence enhancement in presence of Ag(I) salts, while it undergoes quenching in presence of Hg(II). Many other metals did not trigger any appreciable fluorescence variations. This different behaviour towards metal ions is due to the molecular structure: this fluoroionophore has a D<sub>1</sub>-A-D<sub>2</sub> arrangement (D = Donor, A = Acceptor) with D<sub>2</sub> as the selective receptor and D<sub>1</sub> as additional donor, allowing for tuning of the fluorescence properties [2].

Ag(I) enhances fluorescence emission since, after complexation, it can convert D<sub>2</sub> into an acceptor yielding a D<sub>1</sub>-A-A<sub>2</sub> pattern, creating a highly emissive CT species. Hg(II) quenches the fluorescence due to the heavy atom effect. All the other metals that we checked did not give any variations due to low affinity towards the receptor moiety. Both enhancement and quenching can be used for quantification analyses and LODs around 10<sup>-7</sup> M were obtained after preliminary tests.



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## MULTICLASS DETERMINATION OF PESTICIDES IN WHEAT FLOUR BY MEPS FOLLOWED BY HPLC-MS/MS

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The continuous increasing of the population, combined with the steady diminution of the areas designated to the cultivation, has placed the attention on the importance of crop yields, therefore pesticides are used to prevent, destroy, repel, regular or control pests [1]. The wheat is exposed to phytosanitary treatment during planting, growing, harvesting and storage; to avoid serious effects on humans and the ecosystem, for these reasons the European Union by Regulations provided the restrictions on the use and applicability of these substances by laying down strict guidelines, imposing Maximum Residue Limit (MRL) values of pesticides in food and feed.

The aim of this work was the development of a sensitive, accurate method for multiclass analysis of pesticide and fungicide residues in wheat flours; the attention was focused on 16 pesticides with different physico-chemical characteristics and different mechanism of action: acetylcholinesterase inhibitors like organophosphorus, carbamates and neonicotinoids, and inhibitors of ergosterol like imidazoles and triazoles..

The presented method involves a Micro Extraction by Packed Sorbent (MEPS) [2] followed by High Performance Liquid Chromatography coupled to Tandem Mass Spectrometry (HPLC-MS/MS).

The chromatographic separation was conducted using a core-shell column.

For the identification and quantification of the analytes an HPLC-MS/MS equipped with a source TurboIonSpray operating in positive ionization (PI) was used for all analytes. The total run time is 10 minutes.

The quantitative analysis was conducted in Multi-Reaction-Monitoring (MRM), selecting two precursor ion/ion transitions for each analyte.

The acquisition window was divided in four periods to allow the acquisition of all optimized MRM transitions with an appropriate dwell time, in order to improve sensitivity and maintain the quality of the chromatographic peaks, by acquiring a suitable number of points for the shape definition.

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## **DIRECT INJECTION - HPLC ANALYSIS FOR THE DETERMINATION OF FURANIC COMPOUNDS IN OIL AS MARKERS OF SOLID INSULATION DEGRADATION IN POWER TRANSFORMERS**

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The presence of 2-furaldehyde (2-FAL) and related furanic compounds in insulating mineral oils is correlated to thermal degradation and mechanical properties of the Kraft paper used as solid insulation in large electrical equipment (e.g. power transformers). Besides 2-FAL, the main compounds formed by paper degradation are 5-(hydroxymethyl)-2-furaldehyde (5-HMF), 2-furfuryl alcohol (2-FOL), 2-acetylfuran (2-ACF), 5-methyl-2-furfuraldehyde (5-MEF). Nevertheless, 2-FAL is usually the molecule which is found at higher concentrations in the oil, since it is the compound of final degradation of 5-HMF, 2-FOL, 2-ACF and 5-MEF.

The presence of the above-mentioned compounds in the oil is therefore an indication of the health status of solid insulation in power transformers, and their detection represents an important tool for planning maintenance procedure throughout the whole lifetime of the electrical equipment. In order to perform accurate and reliable surveillance of the degradation state of paper, simple, robust and fast analytical methods are required. As regards the determination of furanic compounds in mineral oil, the International Standard IEC 61198 details the analytical methods to be used, which are basically based on a L/L or SPE extraction, followed by HPLC-UV.

The aim of this work is to study the feasibility of the determination of 2-FAL, 5-HMF, 2-FOL, 2-ACF and 5-MEF by direct injection HPLC-UV analysis, without any sample pretreatment.

The method has been developed on a core-shell C18 column, evaluating the effect of sample volume injected, in order to avoid column saturation due to the direct injection of oil. Eluent composition as well as gradient programming have been tuned in order to ensure fast analysis time, and the resolution between 2-FAL and 2-FOL peaks for which the column exhibits similar selectivity. A proper washing procedure has been developed in order to remove the organic compounds which characterize the typical oil profile.

Precision of the method has been calculated by analyzing oil samples from in-service transformers. Accuracy was tested inside three round-robin tests (2012-2014).

## FORENSIC INVESTIGATION ON TEXTILES: CAPABILITIES OF RAMAN SPECTROSCOPY

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Raman spectroscopy is a widely utilized technique in the field of cultural heritage for dating and assessing authenticity of artifacts like paintings, frescoes, manuscripts and scrolls. More recently, attention has been paid to the determination of contaminants in drugs and food [1]. Interesting results have been achieved also in the field of forensic sciences for the analysis of varnishes, narcotics, explosives and textiles [2]. Being a rapid and non-destructive technique that does not require sample preparation, Raman microscopy has been successfully exploited for both the identification of different types of fibers like nylon, cotton and polyamide [3].

Aging is another important factor to be considered when forensic comparison among fibers is carried out. Fibers collected on the crime scene can undergo physical, photochemical, thermal, chemical and mechanical changes, thus making their comparison more difficult.

In this study we demonstrate the capabilities of Raman spectroscopy in distinguishing dyed textiles after aging, in a non-destructive way. The proper optimization of the experimental conditions in terms of choice of laser wavelength, power, signal acquisition time followed by chemometric processing like principal component analysis or discriminant analysis allowed to correctly classify not only textiles produced using similar dyes, but also the samples aged under different conditions. Finally, good values of cross validation demonstrated the feasibility of the proposed technique for forensic science investigations.

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[3] M.M.L. Yu, P. M. L. Sandercock, *J. Forensic Sci.* 57 (2012) 70-74

**ANALYSIS OF DRUGS OF ABUSE: SYNTHETIC CANNABINOIDS AND ALL AROUNDERS**

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The determination of drugs of abuse is an important challenge, and the continuous discovery and commercialization of thousands of designed drugs made the effort very arduous. The two main difficulties from the analytical point of view lie in the doses administered (e.g. LSD, in the order of 100  $\mu\text{g}$ ), and in the introduction on the market of continuously new substances. In particular, in recent years we assisted to the introduction of the so-called “synthetic cannabinoids”, belonging to different chemical classes, often misregulated and freely available from internet (where they are sold as “salt bath”, “spice” or “herbal incense”). Most of them belong to the class of indoles, and the most representative drugs are JWH-018 and the up to date non-regulated adamantly derivative AB-001.

In the present communication, we propose user friendly methods for the on-field qualitative characterization and semi-quantitative determination of some synthetic cannabinoids, based on colorimetric detection of the substances and the analysis of the color intensity (on the RGB scale) with a free i-phone App. This will be a screening test before a deeper analytical characterization of the seized drug.

**LUMICYANO: EVALUATION OF A NEW FLUORESCENT CYANOACRYLATE IN FINGERMARKS DETECTION**

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Fingermarks play a key role in crime scene investigations because their friction ridge pattern can be used for identification purposes. In most cases, fingermarks are invisible and influenced by substrates or environmental factors. Latent fingermarks developed by traditional cyanoacrylate fuming process, often lack contrast with the substrates; therefore further enhancements are required, such as dye staining or powder dusting. This second step, that is part of the conventional detection, aims at improving contrast and at increasing the legibility of details. [1] To avoid the second step, several commercially available formulations of cyanoacrylate have been recently manufactured and marketed as 'one-step' fuming reagents for latent fingerprints revelation. In particular Lumicyano is found to be very promising, combining the cyanoacrylate fuming and the dyeing procedures into a one-step process offering the potential to save time and effort in the detection of latent fingermarks. In this work, a detailed comparative examination between conventional, two-step process (cyanoacrylate fuming followed by staining with Basic Yellow 40) and Lumicyano is proposed for fingermarks detection, in cooperation with the Forensic Science Department (Carabinieri-RIS) of Rome. The study has been conducted on fresh as well as on aged fingermarks (up to 3 months) and applied to non-porous surfaces without changing the fuming chamber settings of forensic laboratories. The fluorescence has been observed either under UV (scenescop, 315-340 nm) or visible (crimescop, 450-550 nm) light irradiation, in order to ensure a good compatibility with the lighting material available within most police forces. The possibility of further DNA detection after marks revelation, has been also investigated.

The results indicate that good ridges clarity and excellent contrast are observed with one step process, concluding that Lumicyano detects fingermarks with equal or better sensitivity and ridge details than currently used cyanoacrylate, extending the acquisition time till three month. Moreover, this study has shown that further enhancement with BY40 after Lumicyano can still be carried out if needed, allowing the identification of marks not revealed in a singol step, for best performing results.

[1] G.Groeneveld, S.Kuijjer, M.DePuit. Science and Justice 54 (2014) 42–48

## **PRESSURIZED LIQUID EXTRACTION FOR THE DETERMINATION OF CANNABINOIDS AND METABOLITES IN HAIR: DETECTION OF CUT-OFF VALUES BY HPLC-HRMS/MS**

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Hair analysis has become a routine procedure in most forensic laboratories since it presents clear advantages: wider time window, non-invasive sampling and good stability of the analytes over time [1]. Cannabinoids analysis in hair is still not straightforward: major challenges arise from low concentration of  $\Delta^9$ -tetrahydrocannabinol (THC) and even lower for the main metabolite 11-nor-9-carboxy-THC (THC-COOH). Furthermore the determination of THC-COOH has shown to be crucial to distinguish among passive drug exposure and active consumption since this molecule is an exclusive product of metabolism and can be considered as marker of drug abuse [2].

The aim of the present work was to develop a sensitive and accurate method for the determination of cannabinoids in hair.

The extraction of analytes from hair (50 mg) is based on an automated pressurized liquid extraction (PLE), followed by SPE: this procedure allows both the reduction of matrix effect and the enrichment of the analytes which is particularly useful for the detection of THC-COOH. The analysis is carried out by HPLC-HRMS/MS with an Orbitrap system. Chromatographic run obtained with a fused-core column provided a good separation of the analytes in less than 4 min.

The whole procedure has been validated according to SWGTOX guidelines. The presented PLE-SPE procedure provides an efficient extraction/sample clean-up with few simple steps and with a minimum use of organic solvents.

To the best of our knowledge, this is the first LC-MS/MS based method that allows the detection of THC-COOH in hair at values lower than the cut-off.

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[2] S. Dulaurent, J.M. Gaulier, L. Imbert, A. Morla, G. Lachatre, Simultaneous determination of THC, cannabidiol, cannabinol and THC-COOH acid in hair using LC-MS/MS, *Forensic Sci. Int.* 236 (2014) 151-6.



**DETERMINATION OF ANTICOAGULANT RODENTICIDES AND  $\alpha$ -CHLORALOSE IN HUMAN HAIR BY ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY AND APPLICATION TO A REAL CASE**

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Anticoagulant rodenticides are the largest group of pesticides used for control of harmful rodents. They are classified into two main groups, depending on their chemical structure: hydroxycoumarine and indandione rodenticides. Their fundamental mode of action is represented by the inhibition of the vitamin K epoxide reductase, which causes blood-clotting alteration, leading to extensive hemorrhages as the ultimate cause of death.

In this study, we developed a UHPLC-MS/MS for the simultaneous determination of 10 anticoagulant rodenticides (coumatetralyl, brodifacoum, bromadiolone, difenacoum, flocoumafen, coumachlor, acenocoumarol, coumafuryl, dicoumarol, warfarin), plus  $\alpha$ -chloralose in human hair, with the scope of detecting potential chronological trace of poisons exposure in clinical and forensic cases. The developed method was applied to a real case of alleged poisoning.

The optimized UHPLC-MS/MS method allowed the simultaneous determination of 10 anticoagulant rodenticides plus  $\alpha$ -chloralose. The whole chromatographic run, comprehensive of the time required for column re-equilibration, was completed in 8.5 min. Retention times ranged between 1.39 min (coumafuryl) and 4.33 min (brodifacoum). In the real case, a segmental hair analyses was performed. Difenacoum was detected in the first hair segment (0-3 cm) at the concentration of 2.9 pg/mg, while  $\alpha$ -chloralose was detected at the concentration of 85 pg/mg. The two remaining, consecutive segments (3-6 and 6-9 cm) showed traces of difenacoum (below the LOQ) and low but quantifiable levels of chloralose (29 pg/mg and 6 pg/mg, respectively).

In conclusion an UPLC-MS/MS method for the simultaneous determination of 10 anticoagulant rodenticides and  $\alpha$ -chloralose in human hair was developed and validated. The method proved to be simple, accurate, rapid and highly sensitive, allowing the simultaneous detection of all compounds. Finally, the method was applied to a real case of difenacoum and  $\alpha$ -chloralose poisoning and proved sensitive enough to detect the occasional exposure to both analytes.

## THE NEVER ENDING STORY OF CANNABINOIDS IN HAIR

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In hair analysis, the distinction between active *Cannabis* consumption and external contamination is a well-known problem. The SoHT recommends the use of cut-offs for THC (50 pg/mg) and its metabolite THC-COOH (0.2 pg/mg) to prove the active consumption. Nevertheless, THC-COOH is frequently not detectable in hair, even if considerable THC concentrations were present and highly sensitive analytical methods were applied. Alternatively, THCA-A has been proposed as a specific marker to prove external contamination and the THC-A/THC ratio as a discrimination factor.

In this study, we analyzed 78 hair samples (60 head and 18 pubic) previously tested positive for THC, in order to (i) evaluate the frequency of THC-COOH positive samples, in comparison to THC positive; (ii) evaluate the possible correlation between THC and THC-COOH levels, and (iii) evaluate the reliability of ratio THCA-A/THC as a valid marker to discriminate between active consumption and external contamination.

A specific UHPLC method coupled to hybrid QqQ-LIT-MS<sup>3</sup> was developed and validated for the detection of THC, THC-COOH and THC-A. LODs for THC, THC-COOH and THC-A were, respectively, 5.30, 0.07 and 0.60 pg/mg. Among 78 samples, 30 tested negative for THC-COOH or below LOQ. Among the 48 positive samples (true active consumers), THC-COOH levels were in the range 0.15-8.93 pg/mg (median: 1.40 pg/mg) while THC and THC-COOH concentrations resulted uncorrelated ( $R^2=0.2238$ ). Among head hair samples, the ratio THCA-A/THC was in the range 0.29-4.95. In these cases, a combined effect of active use and external contamination was likely to account for these THC and THCA-A levels. Among pubic hair, the ratio THCA-A/THC was in the range 0.48-1.55. For these cases, no external contamination is likely to occur and THC and THCA-A levels should be attributed to active use only. Among 30 samples negative for THC-COOH, the ratio THCA-A/THC was in the range 0.68-4.94 (median: 1.99).

Whenever THC-COOH is not detected, the ratio THCA-A/THC may be used to discriminate active consumption from external contamination. A cut-off value of 1.6 is proposed. When THCA-A/THC ratio exceeds 1.6, external contamination may be considered prevalent with respect to active use. Otherwise, absence of THC-COOH combined with THCA-A/THC ratios below 1.6, and low THC absolute levels do not provide conclusive evidences with regard to frequent *Cannabis* consumers identification.

**DETECTION OF 31 STIMULANT, PSYCHEDELIC AND DISSOCIATIVE DESIGNER DRUGS IN REAL HAIR SAMPLES**A. Salomone<sup>1</sup>, G. Gazzilli<sup>2</sup>, D. Di Corcia<sup>1</sup>, E. Gerace<sup>1</sup>, M. Vincenti<sup>1,2</sup><sup>1</sup>Centro Regionale Antidoping e di Tossicologia "A. Bertinaria", Regione Gonzole 10/1, 10043 Orbassano (TO), Italy<sup>2</sup>Dipartimento di Chimica, Università degli Studi di Torino, via P. Giuria 7, 10125 Torino, Italy

Many recreational drugs have been chemically synthesized in the last decade. Among them, a prevalent group is represented by synthetic cathinones, namely substituted phenethylamines compounds, with stimulant or psychedelic activity. However, this new class of substances is not routinely screened in most laboratories. We developed and validated a new analytical UHPLC-MS/MS method in order to detect the most common stimulant, psychedelic and dissociative new drugs in real hair samples. The method was fully validated and applied to 23 real samples taken from proven amphetamines and ketamine abusers and 54 hair samples which had previously been tested negative within regular drug screening in driver's license re-granting. The method proved to be simple, fast, specific and sensitive. The absence of matrix interferences, together with excellent repeatability of both retention times and relative abundances of diagnostic transitions, allowed the correct identification of all analytes tested. Quantitation limits ranged from 3.0 pg/mg for 4-MeO-PCP up to 57.8 pg/mg for 5/6-APB. In the first group, 5 samples tested positive for at least one analyte. MXE was found in 3 cases; mephedrone (4-MMC) in 2 cases. Sporadic findings included 4-MEC,  $\alpha$ -PVP, methylone, 4-FA, MDPV and diphenidine. In the second group, one sample tested positive to methylone. The elusive and changeable profile of the synthetic drugs progressively introduced into the black market makes any tentative study on their diffusion within our communities quite uncertain and incomplete. The use of hair analysis to investigate their diffusion among selected populations of drugs abusers represents a practical tool to obtain significant information with limited investment, due to the relatively high percentage of positive reports. Furthermore, as long as this new class of substances will not be routinely screened in scheduled control programs (e.g. license re-granting), an increasing risk exists that drug consumers will be induced to replace the traditional drugs of abuse with these new synthetic substances.

**DIRECT DRUG TESTING IN ORAL FLUID BY TOUCH SPRAY-MASS SPECTROMETRY WITH MEDICAL SWABS**V. Pirro<sup>1,2</sup>, A.K. Jarmusch<sup>1</sup>, M. Vincenti<sup>2,3</sup>, R.G. Cooks<sup>1</sup><sup>1</sup>Chemistry Department, Purdue University, West Lafayette, Indiana, USA<sup>2</sup>Centro Regionale Antidoping e di Tossicologia "A. Bertinaria", Regione Gonzole 10/1, 10043 Orbassano (TO), Italy<sup>3</sup>Dipartimento di Chimica, Università degli Studi di Torino, via P. Giuria 7, 10125 Torino, Italy

Swab touch spray (STS) mass spectrometry (MS) is a spray-based ambient ionization technique in which a medical swab is used to collect the sample, and ionization is performed directly from the porous swab via electrospray-like (ESI) mechanisms. STS-MS allows for direct, non-invasive and *in vivo* biofluid analysis, *e.g.* oral fluid. The use of commercial medical swabs for both sample collection and ion generation has potential for rapid point-of-care testing in clinical applications, and *in situ* roadside drug testing.

Oral fluid specimens were spiked with a mixture of 14 target drugs and 5 deuterated internal standards. Rayon straight swabs with aluminum wire handle and rayon tip (Copan Diagnostics, IT) were dipped in oral fluid to absorb the specimen (40  $\mu$ L), dried for a short period, and then held in front of the MS inlet. Acetonitrile with formic acid was applied to the swab tip via a fused silica capillary at a steady rate; high voltage (+6 kV) was applied to the metallic swab handle. Data acquisition was started concurrently with high voltage application and formation of a Taylor cone, indicating the onset of ion production. Drugs were detected via sequential product scans in MS<sup>3</sup> using a linear ion trap benchtop mass spectrometer (Thermo Scientific, CA). MS<sup>3</sup> scans proved to provide adequate specificity in the absence of chromatographic separation. Analysis time is rapid (<1 min).

Fourteen drugs, including cocaine, methamphetamines and opiates, were reproducibly identified at ng/mL levels by MS<sup>3</sup> scans, meeting cut-offs sought by international guidelines (LOD values ranged from 1 to 50 ng/mL); Alternative scan types are currently investigated to develop MS-based untargeted drug testing methods. Effects of swab shape, orientation, and distance from the inlet on the formation of the spray plume are currently under study, as well as the optimal properties of the solvent system to generate stable ESI and efficient ionization and inherent matrix effects. The current performance requires extension to develop a multiplexed assay, and refinement in the procedures to meet clinical and legal requirements.

## ELECTRODEPOSITION OF P & N SEMICONDUCTOR LAYERS FOR PHOTOVOLTAIC APPLICATIONS

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Thin film solar cells appear today as a feasible alternative to the silicon wafer-based cells. The main drawbacks in their production are the need of rare and expensive elements (the common thin film cells use CdTe or Cu(In,Ga)Se<sub>2</sub>), as well as the employment of difficult and energy expensive processes for their fabrication. Therefore research in the photovoltaic field needs to focus on alternatives to minimize the exploitation of these rare elements and on more sustainable production processes. Compounds such as Kesterites (CZTS, ternary and quaternary copper and zinc sulfides) could be used in virtue of their semiconductor behavior; also, to simplify the productive process, electrodeposition from aqueous media was proposed; in particular E-ALD (Electrochemical Atomic Layer Deposition) method seems a legit alternative to the high pressure and temperature methods used since today. My work focused on the preparation of two layers of semiconductors, one above the other, to assess the possible usage of the obtained film in the photovoltaic field; first a CuZnS (Kesterite precursor with p electronic proprieties) layer was obtained on an Ag(111) substrate, then the other binary CdS (with n electronic proprieties) layer was grown over. These single compounds and their deposition by means of E-ALD method were largely studied by my research group, but their union to form a junction wasn't tested already. Therefore the first step of my work was the study of the deposition conditions of the CdS on the CuZnS. Using cyclic voltammetry i was able to detect at first the electrochemical inactivity window of the ternary compound, and then the deposition potentials of the Cd and S on the ternary.

To determine if the binary compound shows the underpotential deposition phenomenon above the ternary compound, two deposition methods were tested. The first uses the E-ALD methodology, the second was a simple charge-controlled deposition method.

The obtained samples were characterized morphologically, qualitatively and optically. Scanning electron microscopy (SEM) was used to evaluate both the morphological and the compositional aspects. Composition was also evaluated by x-ray photoelectronic spectroscopy (XPS). In the end diffused reflectance UV-vis spectrometry (DRS) was used to determine the photoadsorbance of the samples.

## ENANTIORECOGNITION TOWARDS L- AND D-DOPA ON EASY-TO-PREPARE INHERENTLY CHIRAL FILM ELECTRODES

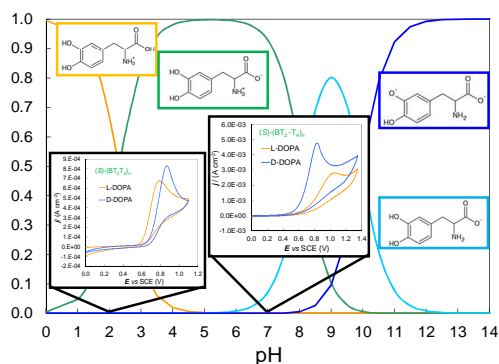
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We have recently shown [1,2] that oligomers endowed with “inherent chirality” display high chirality manifestations plus a pool of unprecedented properties. In particular, in the very last months we have demonstrated that electrooligomerization (especially in ionic liquids) of our inherently chiral monomers on screen-printed electrodes and on glassy carbon tip electrodes affords inherently chiral electroactive films of outstanding enantiodiscrimination ability towards a series of chiral probes of quite different bulkiness and chemical nature (also of pharmaceutical interest like DOPA, common antibiotics and FANS) [3]. The general validity of the “inherent chirality” concept has been confirmed by characterizing monomers and related films based on different atropisomeric biheteroaromatic scaffolds (*i.e.* bis-benzothiophene, bis-indole, and “all thiophene” core). In this work the enantio recognition ability of our smart films towards L- and D-DOPA will be presented focusing on the variation in voltammetric peak separation of the probe enantiomers when changing *i*) the medium (*e.g.* increasing pH, figure below), *ii*) the nature of electrode material and *iii*) the probe carboxylic unit (*i.e.* DOPA methyl ester). The impressive enantiomer peak potential separation combined with the peak current linear dynamic ranges enables to estimate enantiomeric excesses in probe enantiomeric mixtures. Such synthetic electrode surfaces able to neatly discriminate the antipodes of chiral probes as separate peaks are unprecedented in literature, opening the way to the development of efficient chiral voltammetric sensors.

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## TITANIUM AS AN ELECTRODE MATERIAL FOR AMPEROMETRIC SENSORS

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The present contribution aims at investigating the potentialities in electroanalysis of an electrode material very rarely employed in electrochemistry and, in particular, in amperometric techniques, namely Ti. We have experimented that the peculiar nature of Ti leads to quite a different electrochemical behavior with respect to the conventional electrode materials [1,2]. As to the nature of Ti electrodes, a very thin layer (estimable in a few nanometers) of TiO<sub>x</sub> spontaneously forms on the surface in contact with the atmosphere or with an aqueous solution. It should be underlined that the properties of this layer are very different with respect to TiO<sub>2</sub>.

The present contribution focuses on the electrochemical behavior of Au nanoparticles on Ti surface. It is worth noticing that the electrodeposition of noble metal nanostructures on Ti surfaces has been reported rarely in the literature. In particular, Au nanostructures electrogenerated on Ti have never been reported. The deposition of large particles (ca. 1 μm diameter) can be only cited; the density of the nanoparticles and the thickness of the coating are so large that the final system can be considered similar to an homogeneous coating based on pure Au metal.

Electrogenerated Au nanostructures grafted on Ti surfaces impart peculiar electrocatalytic properties. Electrodes consisting of similar bimetallic systems are capable to oxidize glucose in alkaline solutions, but are completely blind to other simple carbohydrates, such as fructose, and to simple alcohols, such as methanol and ethanol. This behavior is significantly different from that of bulk Au: in alkaline solution Au-based materials are excellent electrocatalysts for any carbohydrates and alcohols. Hence, the Ti/Au bimetallic electrode possesses unusual selectivity. The mechanisms through which their properties are exerted are under study.

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**ALKALINE PHOSPHATASE INHIBITION BASED BIOSENSOR FOR 2,4-DICHLOROPHENOXYACETIC ACID (2,4-D) DETECTION**

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2,4-Dichlorophenoxy acetic acid (2,4-D) is an auxinic herbicide with growth regulator activity that has been widely used for controlling broadleaf weeds in cereal grain crops [1,2]. Because of its carcinogenic, teratogenic and estrogenic activity, the presence of residues of 2,4-D in agricultural products and environment can be extremely harmful for both humans and animals [3]. Hence a reliable and rapid technique for its determination is absolutely necessary to ensure both environmental and food safety.

Inhibition based biosensors allow the monitoring of the catalytic activity of the enzyme alkaline phosphatase with the substrate ascorbate 2-phosphate (A2P), in the absence and presence of the inhibitor 2,4-D, using cyclic voltammetry and chronoamperometry [4].

In the present work different screen-printed electrodes (SPE) were used as working electrodes (graphite, graphene, carbon nanotubes and multi-walled carbon nanotubes with Au-NPs) and the immobilization of the enzyme was performed by PVA-SBQ, a photocrosslinkable prepolymer activated by UV irradiation [5]. By comparing the results obtained with the different electrodes, the best performances were observed with the carbon nanotubes/Au nanoparticles electrodes. Under the optimized experimental conditions, with an incubation time of 20 minutes, the biosensor showed a very low limit of detection of 1.0 ppb and the tests carried out on real samples showed an error lower than 10%. The recovery obtained was slightly below 100%, due to the organic and inorganic species present in the sample which could interfere in the 2,4-D determination.

Finally, the reversible nature of the interaction allowed the reuse of the amperometric biosensor about 6 times, with a decrease of signal of only 10%.

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## A NOVEL POLYPHENOL BIOSENSOR BASED ON GREEN ROOM TEMPERATURE IONIC LIQUID AND LACCASE FROM *TRAMETES VERSICOLOR*

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Room Temperature Ionic Liquids (RTILs), composed by organic cations and organic or inorganic anions, have unusual properties such as low volatility, low flammability, high ionic conductivity, high chemical and electrochemical stability [1]. These properties make them very interesting especially for electrochemical applications because of their ability to significantly increase the work potential window ( $V$ ), the electroactive area ( $A_{EA}$ ) and the electron transfer constant ( $k_s$ ), thus allowing the detection of anodic or cathodic peaks, not usually visible.

In this work, we present the development and characterization of a laccase biosensor for polyphenols detection based on a glassy carbon electrode (GCE) modified with COOH-functionalized multiwalled carbon nanotubes (MWCNT-COOH) and IV generation RTILs, composed solely of biomaterials, such as choline and different aminoacids [2]. The so modified electrodes represented a good matrix for the immobilization of Laccase from *Trametes versicolor* (TvL) [3].

The electrodes modified with the different RTILs were electrochemically characterized and all of them showed enhanced values of both  $A_{EA}$  and  $k_s$  compared to unmodified electrodes [4]. The best values were obtained with the RTIL composed of choline (Ch) and phenilalanine (Phe) and therefore this ionic liquid was used for the immobilization of the laccase enzyme.

In the presence of polyphenolic compounds, the electrochemical platform TvL/[Ch][Phe]/MWCNT-COOH/GCE allowed to obtain satisfactory results in terms of sensitivity, selectivity and stability. The biosensor was also tested in real samples of white and red wines and black tea with average recoveries of about 96%.

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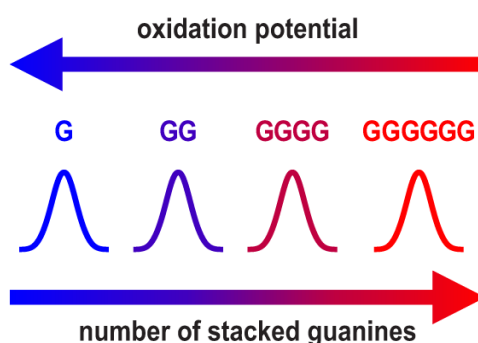
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## DIRECT EXPERIMENTAL DETERMINATION OF THE DELOCALIZED HOLE DOMAINS IN GUANINE-RICH DNA OLIGONUCLEOTIDES: A VOLTAMMETRIC APPROACH

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Graphene has received increasing attention in recent years due to its unique physicochemical properties as high surface area, excellent conductivity and ease of functionalization. In particular, the application of a reduced graphene oxide modified glassy carbon (RGO/GC) electrode were proposed [1] to study the electrochemical responses of different kinds of electroactive compounds (from the free bases of DNA (guanine (G), adenine (A), thymine (T), and cytosine (C)) to the oxidase or dehydrogenase/related molecules systems). The RGO/GC electrode has showed more favorable electron transfer kinetics than glassy carbon electrodes.



Here we report the results of voltammetric measurements on G-rich oligonucleotides containing up to six consecutive stacked G. These sequences have attracted much attention because of their important implications in the DNA damage: a hole originated by an oxidative event can migrate through DNA by *hopping* between neighboring sites or by *superexchange* mechanism. [2] Experimental evidence have shown that sequences containing two or three consecutive G are better hole traps than a single G. [3] So far, no direct experimental determinations of the hole site energies for adjacent stacked G have been reported.

To study the guanine-rich single- and double stranded oligonucleotides, we used a RGO/GC electrode to improve sensitivity for the detection of the progressive lowering of the first voltammetric peak potential  $E_p$  as the number of adjacent guanines increases and the oligomer concentration decreases. The progressive  $E_p$  lowering is a clear-cut experimental evidence of the establishment of delocalized hole domains in G-rich oligonucleotides. The hole stabilization energy obtained

from voltammetric measurements of the oxidation potential's shift amounts to *ca.* 0.1 V for each GG step, significantly lower than that observed and also predicted by computations for AA steps in *ss* A-rich oligonucleotides. [4]

The existence of delocalized domains is a very important issue not only for understanding mechanistic aspects of *long-range* hole transfer but also for the applications that work on DNA's electric properties. [5]

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## **ELECTRO-ANALYTICAL TRACE DETERMINATION OF ACETAMINOPHEN BY ANODIC ACTIVATION OF A GLASSY CARBON ELECTRODE (GCE)**

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This work is inserted in a project, financed by the Compagnia di San Paolo and by the Turin University, focused to the development of sensing devices for the drugs determinations in water samples. The incidence of pharmaceuticals in the environment is a problem of increasing concern, particularly for surface waters [1]. The compounds identified in the environment belong to several classes of human drugs and to date the concentration ranges in natural waters are between 5 µg/L and 0.5 ng/L. Analgesics, anti inflammatories and beta-blockers are the most resistant to the treatment [2]. The development of an electrochemical sensor could allow a faster and easier determination of pharmaceutical compounds and improve the systems of water quality assessment. A simple approach such as the anodic activation of a glassy carbon electrode (GCE) can be used successfully to improve the detection of organic compounds at very low concentration levels. In this work, we observed that the exposure of a GCE to a high potential for a limited time period in the presence of borate/phosphate buffer (pH 9) provides a strongly electro-activated surface. The activated surface was characterized by means of several techniques (SEM, AFM, µ-Raman, XPS). It appeared that the anodization procedure gave rise to a strong oxygen-based functionalization that did not affect morphologically the electrode surface. The activated electrode was applied to the electroanalysis of acetaminophen by differential pulse voltammetry. The analytical performance of the electrode (limits of detection and quantification) was determined in borate/phosphate buffer (pH 9) obtaining: LoD=2·10<sup>-9</sup> M, LoQ=9·10<sup>-9</sup> M and a linear response up to 1.5·10<sup>-7</sup> M. The electrode was also tested with tap and lake water samples spiked with 5·10<sup>-8</sup> M acetaminophen.

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## EVALUATION OF AN ELECTROCHEMICAL ROOM TEMPERATURE IONIC LIQUID-BASED MICROPROBE FOR GAS ANALYSIS

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A simple electrochemical microprobe (EMP) is here proposed for gas analysis. The proposed probe consists of two platinum fibers of 25 and 300  $\mu\text{m}$  in diameter encased into a theta glass pipet, which allows obtaining a two-electrode cell, in which the smallest fiber acts as the working electrode. The finished EMP presents a couple of disk shaped microelectrodes with a well-defined and controllable surface area. Ion conductivity between the two electrodes is ensured by a thin film of room temperature ionic liquid (RTIL) produced by a simple dip-coating procedure. This room temperature ionic liquid-based electrochemical microprobe (RTIL-EMP) is, preliminarily, investigated by using ferrocene as an electroactive species to ascertain either the stability of the RTIL film that adheres onto the tip surface when it is left in the gas phase, or the mass transport characteristics that apply to the working microelectrode surface. The RTIL used in this work is 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][NTF<sub>2</sub>], which allows liquid films of thickness as small as 30  $\mu\text{m}$  to be obtained. Under such conditions an equilibration time of a few seconds is needed to achieve stable and reproducible voltammetric and chronoamperometric responses. Long term stability, reproducibility and recover of the RTIL film layers to the initial conditions are investigated in detail. Finally, the suitability of the RTIL-EMP for gas analysis is verified by using oxygen as an electroactive species. To this purpose the RTIL-EMP is exposed to different synthetic O<sub>2</sub>/N<sub>2</sub> mixtures in an air tight vessel and current responses are examined as a function of O<sub>2</sub> concentration. Regression analysis of the experimental points indicates a satisfactory linear trend with correlation coefficient of 0.996.

## ELECTRODEPOSITION OF Pt NANOPARTICLES ON POLYPYRROLE NANOWIRE NETWORK

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Conducting polymer (CP) nanostructures have attracted a huge scientific and technological interest during the last decades because they have the merit of combining features of highly conjugated polymer with ones of nanomaterials, as large surface area, size, and quantum effect [1]. Polypyrrole (PPy) is one of the most widely used CPs due to its high electronic conductivity, biocompatibility and good stability in air and aqueous media, and many efforts for developing novel strategies for the manufacture of PPy nanostructures with controlled morphology have been done [1]. While confining electrochemical oxidation of monomers in porous hard templates has been widely explored to this aim, template-free approach seems desirable for avoiding multistep and post-treatment processes [2]. During the last years, PPy application field was further enlarged by its use in composite systems integrating materials such as redox mediators and metal nanoparticles etc., with the aim to exploit properties of the individual components gaining a synergistic effect. A few examples have been reported on systems composed of PPy and platinum nanoparticles for applications as biosensors [3] and fuel cells [4], not being focused on the optimization of composite systems.

The purpose of this work is to perform a systematic investigation of electrochemical deposition of platinum nanoparticles within a network of PPy nanowires, fabricated by an electrochemical template-free approach. Different methods of platinum electrodeposition (i.e. Cyclic Voltammetry, potentiostatic deposition and potential step deposition) are carried out on PPy nanowires with different morphologies, achieved by modifying synthesis conditions (i.e. electropolymerization time and pH of the polymerization solution).

The aim of this study is to identify conditions allowing the enhancement of the electrochemical properties of the composite system Pt/PPy nanowires for perspective catalytic applications in sensors or fuel cells.

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## ON THE INTERACTION OF RISEDRONIC ACID WITH MAJOR COMPONENTS OF BIO AND NATURAL FLUIDS

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In this contribution we report the results of a study on the acid-base properties of Risedronic acid (RA, 1-hydroxy-1-phosphono-2-pyridin-3-yl-ethyl phosphonic acid). This molecule belongs to the class of biphosphonates (BPs), which are mainly used for the treatment of different bone diseases and calcium metabolism disorders. Recently, BPs have been used as growth inhibitors for parasitic diseases like malaria and in crystal engineering studies. Although these molecules have been available for decades, a detailed understanding of their most important physicochemical properties under comparable conditions is lacking. In this contribution, the solubility and the acid base properties of RA were studied in  $\text{NaCl}_{(\text{aq})}$  (0.1 - 5 mol dm<sup>-3</sup>),  $(\text{CH}_3)_4\text{NCl}_{(\text{aq})}$  (0.1 - 3 mol dm<sup>-3</sup>) and  $(\text{C}_2\text{H}_5)_4\text{NI}_{(\text{aq})}$  (0 - 1 mol dm<sup>-3</sup>) at different temperatures 283.15 - 310.15 - 318.15 K. In these three salts, the solubility of RA is very different, for instance in  $\text{NaCl}_{(\text{aq})}$  the total solubility increases with increasing the salt concentration up to  $m_{\text{NaCl}} \sim 2 \text{ mol kg}^{-1}$ , and for  $m_{\text{NaCl}} > 2 \text{ mol kg}^{-1}$  the solubility slightly decreases, whereas an opposite trend is observed in  $(\text{CH}_3)_4\text{NCl}_{(\text{aq})}$  and  $(\text{C}_2\text{H}_5)_4\text{NI}_{(\text{aq})}$ . From the analysis of the solubility measurements it was possible to determine the Setschenow and the activity coefficients of the neutral species. The protonation constants ( $\log K_i^{\text{H}}$ ) of

RA were then determined in similar experimental conditions. The stability constants of RA with  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were studied in NaCl at different ionic strengths (0.1 - 5 mol dm<sup>-3</sup>) and temperatures (283.15 - 310.15 - 318.15 K). For these systems, *Ab initio* computational studies, considering explicit water molecules, have been also provided to guess the conformation of the complex species. To enlarge the knowledge about this system another ionic medium was considered, namely synthetic sea water (SSW), in which the solubility of RA, the protonation constants and the stability constants of mixed  $\text{Mg}^{2+}/\text{Ca}^{2+}/\text{RA}$  species at  $T = 283.15$  and  $298.15 \text{ K}$  were determined. The dependence of equilibrium constants on ionic strength was analyzed considering (i) the variation of the activity coefficients with ionic strength (SIT model), and (ii) the formation of weak complexes between the ions of the supporting electrolytes with the ligand species (a weak complexes model).

## GLUCONIC ACID: THERMODYNAMIC PROPERTIES AND COMPLEXING ABILITY TOWARDS METAL CATIONS

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Gluconic acid is a noncorrosive, nonvolatile and nontoxic mild organic acid, derived from glucose by a simple oxidation reaction (enzyme glucose oxidase and glucose dehydrogenase). Gluconic acid and its derivatives have wide applications in food, medical, pharmaceutical and environmental fields. It is a good chelating agent at alkaline pH and its action is comparatively better than EDTA, NTA and other ligands. As consequence of the importance and the wide use of this natural ligand, a detailed speciation study has been carried out. In particular, the acid-base properties of the ligand were studied in NaCl and NaNO<sub>3</sub> aqueous solutions at different ligand concentrations, ionic strengths ( $0.5 \leq I(\text{NaCl}) / \text{mol dm}^{-3} \leq 4.0$  and  $0.15 \leq I(\text{NaNO}_3) / \text{mol dm}^{-3} \leq 2.9$ ) and temperatures ( $283.15 \leq T/\text{K} \leq 318.15$ ).

The complexing ability of gluconic acid (L) was studied towards two metal cations, Zn<sup>2+</sup> and Sn<sup>2+</sup> by two different analytical techniques: potentiometry and voltammetry, that allowed the determination of the ML and ML<sub>2</sub> species for both systems, together with, in certain conditions of ligand concentration ( $c_L > 0.1 \text{ mol dm}^{-3}$ ), various M(OH)<sub>i</sub>L<sub>k</sub> species.

The formation constant values of the Sn<sup>2+</sup>/L<sup>-</sup> species are higher than the corresponding Zn<sup>2+</sup>/L<sup>-</sup> species.

The formation of the insoluble species Sn(OH)L and Zn(L)<sub>2</sub> was evidenced at pH ~ 5.0 and 7.0, respectively, and the values of their total and specific solubility were determined in NaCl and in NaNO<sub>3</sub> aqueous media. The solubility measurements allowed us to determine the Setschenow and the activity coefficients of the neutral species. The dependence of the protonation and formation constants on ionic strength was modeled by means of the extended Debye-Hückel equation and the Specific Ion Interaction Theory (SIT).

Calorimetric experiments were performed to obtain the protonation and Sn<sup>2+</sup> complex formation enthalpy changes at different ionic strengths in NaCl<sub>(aq)</sub>.

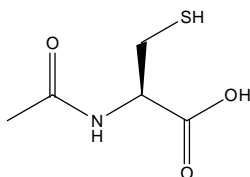
The choice of these two cations is related to the fact that zinc-gluconate is used as an ingredient for treating various diseases caused by zinc deficiencies, such as mental lethargy and skin changes, whilst some Sn<sup>2+</sup> compounds are employed in different industrial fields, therefore, the knowledge of the complexing ability of a natural, nontoxic chelating agent as the gluconic acid is of great importance from an environmental point of view (as in remediation of polluted sites).



## INTERACTION OF N-ACETYL-L-CYSTEINE WITH DIVALENT METAL CATIONS

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N-acetyl-L-cysteine (NAC)

NAC is a drug that was first reported to have clinical benefit in the early 1960s. For several decades, it has been used as antioxidant, as a mucolytic agent, for the treatment of cancer, HIV infections, cardiovascular diseases and metal toxicity. Most of these therapeutical uses are due to its metal binding properties. Despite this, literature thermodynamic data on its binding ability towards metal or organometal cations are not complete.

Here we report a thermodynamic study on the interaction between NAC and  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ , at  $I = 0.1 \text{ mol dm}^{-3}$  in NaCl and  $t = 25^\circ\text{C}$ . Investigations were performed by potentiometric and UV spectrophotometric titrations and, for both techniques, were preceded by the evaluation of the acid-base properties of the ligand.

The speciation models obtained for NAC- $\text{Pb}^{2+}$  and - $\text{Zn}^{2+}$  systems include the formation of the same three species,  $\text{ML}_2$ ,  $\text{ML}_2\text{H}$  and  $\text{MLOH}$ . Owing to the high stability of NAC- $\text{Hg}^{2+}$  species, the potentiometric study on this system was performed by using a competitive ligand (NaI), as reported in a previous paper on S donor ligand- $\text{Hg}^{2+}$  interactions [1]. For the NAC- $\text{Hg}^{2+}$  system, in addition to the  $\text{ML}_2$ ,  $\text{ML}_2\text{H}$  and  $\text{MLOH}$  species, obtained for NAC- $\text{Pb}^{2+}$  and - $\text{Zn}^{2+}$ , the formation of  $\text{ML}$  and  $\text{MLH}$  species was evidenced. Stability of these species is very high, as an example for  $\text{HgL}$ ,  $\log \beta = 31.64$  at  $t = 25^\circ\text{C}$  and  $I = 0.1 \text{ mol dm}^{-3}$  in NaCl. NAC- $\text{Cu}^{2+}$  interaction was investigated only by means of UV spectrophotometry. For this system the use of potentiometry was not possible owing to the formation of sparingly soluble species.

On the basis of the formation constants and speciation profiles, the sequestering ability of NAC towards the different metal cations was quantitatively evaluated by determining an empirical parameter that numerically represents the ligand concentration necessary to sequester 0.5 of metal ion fraction.

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## MODELLING OF PROTONATION CONSTANTS OF HALLOYSITE CLAY NANOTUBES IN VARIOUS AQUEOUS MEDIA, AT DIFFERENT IONIC STRENGTHS

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In the last decade nanoparticles have assumed more and more importance because of their particular properties mainly due to the nanometer-scale dimensions that confer them a large surface/volume ratio. Among nanomaterials one of the most studied is the halloysite that, as well as the other natural clay minerals is safe for human and environmental friendly. Halloysite is abundant and cheap and is present in large deposits worldwide like those in New Zealand, France, Belgium and China [1,2]. It is similar to kaolin but has a hollow tubular structure that can be attributable to particular crystallization conditions. Typically, halloysite nanotubes (HNTs) are formed by 15 – 20 aluminosilicate layers, has a length of  $1 \pm 0.5 \mu\text{m}$  and inner and outer diameters of  $\sim 15$  and  $50 - 70 \text{ nm}$ , respectively [1,2]. In each layer the SiOH and the AlOH groups are disposed on the external and the internal surfaces, respectively. As consequence, the chemistry of the lumen and of the outer surface of HNTs is completely different. In particular, in each nanotube the inner surface is positively charged and the outer surface has an excess of negative charges in a wide pH range. The particular structure of HNTs makes this kind of clay mineral very useful for different purposes and several papers and reviews have been published on their different applications [1-3]. The behavior of HNTs in all these applications is strictly related to their acid-base properties that here have been studied by ISE- $\text{H}^+$  potentiometric titrations in several interacting and non interacting ionic media, in the range  $0.025 \leq I \text{ mol L}^{-1} \leq 1.000$ , at  $T = 25^\circ\text{C}$ . Two functional groups indicated with  $\text{HNT}_1$  (SiOH) and  $\text{HNT}_2$  (AlOH) were considered in the analysis of the experimental data. Potentiometric data related to the  $\text{HNT}_1$  groups were processed with four different models previously used for the study of the acid-base properties of natural and synthetic polyelectrolytes: Högfeltdt, Linear, modified Henderson-Hasselbalch and diprotic like models [4]. The acid – base behavior of  $\text{HNT}_2$  groups were well defined by one protonation constant calculated by processing the potentiometric titration data with the computer programs STACO and BSTAC.

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## **Fe<sup>III</sup>, Al<sup>III</sup>, Cu<sup>II</sup> AND Zn<sup>II</sup> COMPLEX FORMATION STUDIES WITH BIS-KOJIC ACID DERIVATIVES.**

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Different elements (e.g. Fe, Zn, Cu) are essential for the growth and development of organisms and cells. In healthy humans, homeostatic and buffer mechanisms maintain the concentrations of these free metal ions at a physiological level, preventing their abnormal decompartmentalization, release and trafficking [1].

Non-essential metal ions can enter the body due to environmental exposure and to the administration of metallodrugs for therapy/diagnosis purposes. Once entered, they compete with biometals, generate oxidative stress and deregulate several enzyme systems, causing different pathologies. Medicinal inorganic chemistry deals with the introduction of metal ions in the body, and their removal or passivation, namely through the design of tailored chelating agents [1].

Kojic acid (KA) is a non-toxic antifungal and antibacterial agent that has been extensively studied for its tyrosinase inhibitory and metal coordination properties. In our project we synthesized different bis-kojic acid derivatives as metal chelating agents and determined the stability constants of their Fe<sup>III</sup>, Al<sup>III</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> complexes with the use of different experimental techniques (potentiometry, UV-Vis, ESI-MS and NMR) [2-6].

The main purpose of this communication is to present the influence on complex formation of the linker between the two kojic acid units. The impact of the length and composition of the linkers both on pK values of the free ligand and on the stability of the metal complexes, will be discussed.

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## KINETICS OF METAL ION ACCUMULATION ON THE RESIN CHELEX 100

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The chelating resin Chelex 100 has found a large number of applications in many fields of biology and analytical chemistry; one of the most recent ones is its use in the binding layer of DGT (Diffusive Gradients in Thin films) devices [1], which are designed to probe metal availability in natural waters. Despite its importance, only a limited number of experimental and modelling studies addressing the kinetics of metal uptake on chelating resins have been reported in the literature [2]. In particular, the role of mass transport mechanisms, and the influence of ionic strength or stirring rate have not been completely investigated to date.

A simple method, based on the use of Cd Ion Selective Electrodes, was developed to monitor the extent of reaction as a function of time. Compared with periodic subsampling and off-line analysis with ICP-MS, ISE potentiometry proved to be an accurate method, particularly useful in the case of fast uptake kinetics. If competing ligands are present in solution, the coupling of potentiometric and ICP-MS analysis allows to measure in parallel the evolution of total and free metal ions concentrations, thus providing speciation data in real time.

This work presents data on the sorption kinetics of two cations of environmental interest, Cd(II) and Ni(II) on Chelex 100 resin as a function of experimental variables like pH, ionic strength, initial metal ion concentration, mass of resin beads, and stirring rate. Finally, the results are interpreted by means of a newly developed kinetic model involving control by both external film and intraparticle diffusion. The conclusions provide a further insight into the mechanisms underlying the performance of DGT devices in environmental samples.

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## GOLD MICROTUBES ASSEMBLING ARCHITECTURE FOR AN IMPEDIMETRIC GLUCOSE BIOSENSING SYSTEM

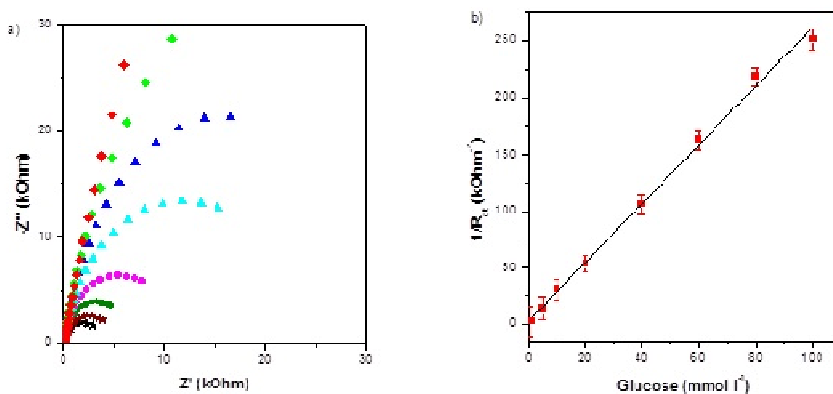
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A glucose impedimetric biosensor was assembled using a gold microtubes (Au $\mu$ Ts) architecture. A platinum (Pt) electrode (diameter 3 mm) was coated by gold microtubes, synthesized via electroless deposition within the pores of polycarbonate particle track-etched membranes (PTM).

This platform was successfully used to deposit polypyrrole overoxidized film (OpPy) and to verify the possibility of developing a biosensor using OpPy, the characteristics of the H<sub>2</sub>O<sub>2</sub> charge transfer reaction were studied before the enzyme immobilization. This composite material could be suitable in devices as biosensors based on oxidase enzymes, just because hydrogen peroxide is a side-product of the catalysis and could be directly related to the concentration of the analyte. Finally, a biosensor consisting in a Pt electrode modified with Au $\mu$ Ts, OpPy and glucose oxidase was assembled to determine the glucose [1].

The most important result of this biosensor was the wide linear range of concentration, ranging from 1.0 to 100 mM (18 mgdl<sup>-1</sup>-1800 mgdl<sup>-1</sup>), covering the hypo- and hyperglycemia range, useful in diabetes), with limit of detection (LOD) of 0.1 mM (1.8 mgdl<sup>-1</sup>) and limit of quantification (LOQ) 1.0 mM (18 mgdl<sup>-1</sup>).



**Figure 1.** a) Impedance response of GOD/opPy/Au $\mu$ Ts/Pt electrode in solutions of glucose in phosphate buffer at pH 7, for concentrations ranging from 1.0 mM, to 100.0 mM, b) Calibration curve  $1/R_s$  vs. glucose concentrations

[1] C. Bianchini, D. Zane, A. Curulli, (2015) Sensors & Actuators B accepted

## SMARTPHONE-BASED COLORIMETRIC ASSAY FOR CA125 CANCER BIOMARKER DETECTION

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There is an urgent need for cost-effective point-of-care (POC) instruments with homogenous technical requirements as well as more flexible devices for biomarker diagnostics in clinical settings. Due to the recent advances in smartphone features (such as capability, processing power, hardware and software), it becomes a promising tool for mobile diagnostic and bio-analytical POC tools. Colorimetric detection is an ideal method for miniaturization and POC biosensor development because of its inherent sensitivity and simplicity.

In this work, we have developed a simple and accurate affisensor based on a colorimetric immunoassay method coupled to a smartphone in order to detect quantitatively the ovarian cancer antigen 125 (CA125). The affisensor is based on a sandwich immunoassay in which the primary antibody was immobilized by spotting the antibody solution on nitrocellulose membrane. Subsequently, the spots were incubated with CA125 antigen followed by affinity reaction with a secondary antibody conjugated to gold nanoparticles (AuNPs). The silver enhancement reaction was introduced to magnify the signal detection. The experimental data show that this reaction can be observed by the naked eye. The formation of gold-silver nanoparticles results in a different grey colour, depending on CA125 concentration. The smartphone camera was used as colour detector, for image acquisition and data handling via a specific application.

The parameters involved in each step of the affisensor design were optimized. The performance of the immunoassay in terms of sensitivity, reproducibility and selectivity was studied.

Under optimal conditions, a linear response was obtained in the range of 60 – 1000 U/mL, which is also the important range from clinical point of view. The method is simple, fast, and could be performed without requiring highly skilled operating personnel and expensive instrumentation allowing point-of-care analysis with reductions in cost and response time.

## NOVEL APPROACHES FOR ALZHEIMER'S DISEASE BIOMOLECULAR DIAGNOSIS

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We will present preliminary results of the project entitled "Sviluppo di Biosensori di affinità a base di un nuovo recettore aptamerico, per la diagnostica molecolare della malattia di Alzheimer" within the Vinci program 2013, funded by the Università Italo-Francese. The aim of this project is the development of Surface Plasmon Resonance (SPR) aptasensing based on novel bioreceptors for AD biomarkers, i.e. tau protein, with application in AD molecular diagnostic. Eventually an immunosensor for tau protein is developed for comparing aptasensor and immunosensor performances in terms of the main analytical parameters. The work presented will be relative to the results achieved in the development of the aptamer for tau, performed at the Université Grenoble alpes, and the tau immunosensor development, done at Università di Firenze. We addressed Alzheimer's disease (AD) since it is a widespread pathogenic condition which cause memory and behaviour impairment in elderly people because of the accumulation of amyloid beta peptide and tau protein [1]. Since up to now therapeutic intervention is not able to stop the progression of the pathology, early diagnosis assumes crucial role to slow down cognitive decline in AD patients. After revising clinical criteria of AD diagnosis in 2007 [2], three core biomarkers have been accepted as supportive criteria for the identification of the pathology: amyloid beta peptide (A $\beta$ ), protein tau (t- $\tau$ ) and phosphorylated tau (p- $\tau_{181}$ ) After many years of research focused on A $\beta$ , tau protein has emerged therapeutic target for the treatment of AD. Moreover increasing of tau levels in biological fluids is associated with several pathogenic processes involving neurodegeneration.

We started the development of the SPR immunosensor using bare gold biochip functionalised via self-assemble monolayer with monoclonal antibodies (Mab) against tau protein. Calibration in bstandard solution and in simulated Cerebro Spinal Fluid (CSF) simulated matrix are reported.

In order to develop the aptasensor, aptamer selection started thanks to Capillary Electrophoresis-SELEX (CE-SELEX). Two strategies were tested with very different results. Conventional SELEX was unable to produce significant evolution in the oligonucleotides population, thus a non-SELEX approach was tested. Such method, developed by Berezovski and colleagues [3], is faster than conventional SELEX, and may produce significant evolution when PCR by products are formed.

Future work is directed to improve immunosensor limit of detection, and, after aptamer sequencing, to the development of the tau aptasensor. SPR imaging

(SPRi), with its ability to monitor up to thousands biomolecular interactions [4] might also be used to compare the performances of both bioreceptors at the same moment in the same platform.

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## **DEVELOPMENT OF A SURFACE PLASMON RESONANCE BASED BIOSENSOR FOR OVALBUMIN DETECTION IN WINES**

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Food allergy is nowadays regarded as a problem of public-health relevance, the main concern being the unintentional exposure of allergic consumers to the offending ingredient through allergen-containing food. Rapid diagnostic tools are increasingly being requested by food companies to verify the efficiency of their management schemes for food safety. Although no specific reference analytical method for the determination of fining agent proteins has been prescribed, the international Organization of Vine and Wine (OIV) resolution 427-2010 modified by the OIV/COMEX 502-2012 set up the analytical requirements to be fulfilled by methods under development. In particular, ELISA methods must comply with the detection limits and the quantification limits of  $\leq 0.25$  and  $0.5$  mg/L, respectively.

In the present communication, the development of a surface plasmon resonance (SPR)-based biosensor tailored to the fast detection of egg related fining allergens in wines is described. Ovalbumin (OVA) was chosen as target protein to be monitored due to its highest abundance in the egg white (EW) powder, a typical fining agent used by the winery industry to promote wine clarification. A direct assay was designed, basing on the use of polyclonal anti-OVA antibody as bio-specific receptor. After the fine tuning of all parameters able to influence the final response, the assay was tested in a direct assay for OVA in commercial wines artificially contaminated with EW powder. The devised assay allowed to trace, in a short analysis time and with a minimal sample pre-treatment, the presence of egg allergens at the lowest concentration comprised between  $0.03$  and  $0.2$   $\mu\text{g/mL}$  [1].

This research was funded by the Project S.I.Mi.S.A.: “Innovative tools for the improvement of food safety: prevention, control and correction”-P.O.N. Ricerca e competitività 2007–2013 per le Regioni della Convergenza Codice Progetto PON02\_00657\_00186\_3417512/1. The work was also partly funded by the Italian Ministry of Economy and Finance to the CNR for the project “Innovazione e Sviluppo del Mezzogiorno-Conoscenze Integrate per Sostenibilità ed Innovazione del Made in Italy Agroalimentare–Legge n.191/2009”.

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**NANOPARTICLES MODIFIED SCREEN PRINTED ELECTRODE FOR ELECTROCHEMICAL DETERMINATION OF COD.**

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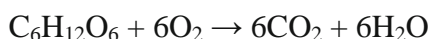
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The Chemical Oxygen Demand (COD) is a parameter widely used to determine organic pollutants in water and is defined as the number of oxygen equivalents necessary to oxidize the organic compounds. The standard method for COD measurement (the dichromate titration) suffers from several inherent drawbacks such as the long time of the process and the consumption of toxic chemicals. Hence, interest is growing towards those methods employing electrochemical oxidation of organic compounds, as they allow to dispense with toxic reagents and above all to perform a continuous determination.

In this work a new electrochemical method for COD measurement has been developed based on direct oxidation of organic molecules on suitably modified electrodic surfaces.

In particular, we have developed various sensors based on modified working electrode surfaces obtained by electrodepositing copper and/or nickel oxide nanoparticles onto several commercial screen printed electrodes. Glucose was used as the standard compound for COD measurements:



The metallic nanoparticles catalyze the oxidation of the glucose, as well as of different organic pollutants, and make the detection possible at relatively low potential, also in presence of chloride as interferent. The analytical parameters were optimized and the results obtained highlight how the electrodeposition of different metallic nanoparticles onto several screen printed electrode surfaces can influence the selectivity and sensitivity towards the COD detection in real matrices, via electrochemical method. The results were compared with those obtained by the standard method and showed a good agreement. These findings provide an interesting strategy to obtain a simple, cheap, portable and eventually continuous sensor for COD measurement.

## **ETHANOL DETERMINATION IN WINE AND BEER USING A DIRECT CATALYTIC METHANOL FUEL CELL (DMFC)**

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It was investigated the feasibility of using a small catalytic direct methanol ‘fuel cell’, for analytical purposes (originally constructed for the purpose of obtaining energy from methanol or ethanol).

The aim was to see whether this kind of device can be effectively used for ethanol and methanol determination. To this end, the potential increase at the open circuit voltage, that occurs at two electrodes of the cell, was observed and lastly the maximum potential obtained after each alcohol addition read off. We thus experimentally demonstrated that it is possible to obtain calibration curves for both methanol and ethanol. The second research step was to repeat the above tests but this time using a potentiostat and recording the current supplied by the cell, after it had reached a stationary value, at different concentrations of ethanol or methanol, after optimizing the applied potential, operating at fixed alcohol concentration. The current variations thus obtained have been reported as a function of the concentration of the alcohol tested, obtaining new calibration curves.

A comparison of the main analytical data are not very different using two formats. On the other hand, the measurement time is much lower when operating in potentiostatic format; lastly, sensor lifetime is in any case greater than 3 months. Lastly the fuel cell was utilized for ethanol determination in four different commercial samples of wine and three of beer. Results were compared with those obtained using biosensors recently developed by our research group for ethanol determination [1].

Finally tests were carried out, again measuring the current supplied, although also using enzymes, such as catalase, alcohol oxidase and alcohol dehydrogenase inserted inside the anode section of the fuel cell, contained in a small dialysis bag immersed in the ethanol or methanol-water solution.

Results indicated that the presence of one of the above-mentioned enzymes, particularly alcohol dehydrogenase, actually improves analytical performances of the fuel cell.

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**STRUCTURE-SWITCHING DNA SENSORS BASED ON TRIPLE HELICES FORMATION**

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DNA-based sensors that shift between two or more conformations upon binding to a specific target, or for a change in the environment, can be used to build robust, sensitive, and specific sensors. Among the various structure-switching strategies employed by DNA-based sensors, those based on the formation of triple helices structure seem very interesting and promising. Exploiting the features of parallel triplex structure, we first designed and explored a DNA clamp-like molecular receptor that recognizes a specific complementary oligonucleotide target through two recognition elements that both bind and recognize the target. These two distinct recognition elements are based on Watson–Crick and triplex-forming Hoogsteen interactions, which lead to the formation of a triplex DNA structure. We fully realize and exploit the advantages of such molecular “double-check” mechanism, by adapting this clamp-like sensing strategy to a DNA-based electrochemical biosensor. We demonstrate that this target-binding mechanism can improve both the affinity and specificity of recognition as opposed to classic probes solely based on Watson–Crick recognition. By using electrochemical signaling to report the conformational change, we demonstrate a signal-on E-DNA sensor with up to 400% signal gain upon target binding. We were able to detect with nanomolar affinity a perfectly matched target as short as 10 bases. Moreover, exploiting the pH-dependence of parallel triplex structure we have designed programmable DNA-based nanoswitches whose closing/opening can be triggered over specific different pH windows. These nanoswitches form an intramolecular triplex DNA structure through pH-sensitive parallel Hoogsteen interactions. We demonstrate that by simply changing the relative content of TAT/CGC triplets in the switches, we can rationally tune their pH dependence over more than 5 pH units. The ability to design DNA-based switches with tunable pH dependence provides the opportunity to engineer pH nanosensors with unprecedented wide sensitivity to pH changes.

## TESTING OF ALGAL TOXINS IN DRINKING, FRESH AND SEA WATER SAMPLES WITH AN OPTIMIZED COLORIMETRIC PHOSPHATASE INHIBITION ASSAY

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Okadaic acid (OA) is a marine toxin produced by *Dinophysis* and *Prorocentrum* and is responsible for causing diarrhetic shellfish poisoning (DSP) to humans after ingestion of contaminated shellfish. Since contamination of bivalves has become a serious economic concern for the shellfish industry, the European Food Safety Authority (EFSA) has established the maximum permitted level of OA as 45 µg/kg of mussels in order to protect consumer health [1].

Microcystins (MCs) are a class of hepatotoxins produced by cyanobacteria such as *Microcystis*, *Oscillatoria* and *Anabaena* usually found in lakes, water reservoirs and recreational facilities. For this reason, MCs are a drinking water public health issue with a provisional drinking water guideline of 1 µg/l for microcystin-LR (WHO, 1998). On the basis of a widely conservative approach towards the protection of the humans' health the value of 1 µg/l would be referred to the sum of the toxin concentrations present in the sample, considered as equivalents of MC-LR [2]. The mechanism of action of these toxins is based on the inhibition of protein phosphatase type 2A (PP2A) by the toxins. The degree of inhibition of the PP2A enzyme can be used as a measure of toxin concentration in aqueous solution sample.

In this work we propose a colorimetric assay in which the activity of protein phosphatase-2A is determined by measuring the rate of color production from the release of yellow *p*-nitrophenol using *p*-nitrophenyl phosphate as the substrate. In the presence of MCs or OA enzyme inhibition occurs and consequently the rate of color production decreases proportionally to the concentration of the toxin.

The optimized colorimetric assay was also used to test different water samples, without preconcentration step, in terms of recovery for both toxins. An optimal average recovery of 98% and 99% was calculated for MC-LR and OA, respectively.

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## **ALLOSTERIC DNAZYME/RNAZYME FOR HIGH SPECIFIC DETECTION OF BIOLOGICAL AND ENVIROMENTAL TARGET**

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Conformational-switching aptazyme, also known as allosteric DNA/RNAzyme, are proving increasingly useful in nanobiotechnology, particularly in biosensing applications. Such sensor elements generally fuse a molecular recognition element (aptamer) with a catalytic signal generator.

Here we demonstrate a general strategy for the rational design of nucleic acid catalysts that can be allosterically activated by specific biological and enviromental targets.

More specifically, we firstly have combined a catalytic DNAzyme sequence and the consensus sequence recognized by specific transcription factors and we have designed and characterized two peroxidase-like DNAzymes whose activities are triggered upon binding either TATA binding protein or the microphthalmia-associated transcription factor.

We have also developed novel ligand-sensing, conformational switching ribozyme for the detection of palitoxin and domoic acid which represent emerging marine water pollutants.

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## **A MULTI-APTASENSORS SYSTEM FOR THE DETECTION OF MARINE ALGAL TOXINS**

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Some marine algae can produce harmful toxins that accumulated in vectors have impact human health through the consumption of contaminated shellfish and finfish or through water or aerosol exposure. Therefore, early detection of algal toxins is an important aspect for public safety and natural environment [1]. For this purpose, we are developing biosensors that can be used in a novel automated networked system that will enable real-time in-situ monitoring of marine water chemical and ecological status in coastal areas.

The challenging purpose is the development of a multi-aptasensors system which can in principle detect simultaneously several toxins in the same box, functionalizing aptamers with different fluorophores/quencher emitting at different wavelengths in order to distinguish simultaneously the different toxins. By introducing organic fluorophores into conformationally labile regions of the aptamers, it is possible transduce ligand binding into a change in the chemical environment of the fluorophore and hence to a change in fluorescence intensity [2].

The authors would like to acknowledge the financial support from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no 613844.

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## CHITOSAN/CARBON BLACK NANOPARTICLES AS BIOCOMPATIBLE SCAFFOLD FOR ENZYME-BIOSENSORS DEVELOPMENT

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The modern electroanalytical chemistry increases its successes thanks to the synergy between the wide world of nanomaterials, and the progresses in the electronic field, afford several advantages such as the miniaturization of the devices, the reduced costs and an easier mass production. One of the most representative example are the Screen-printed electrodes (SPEs), successful sensors due to their low background, wide potential window and easiness of surface modification. They can be integrated in a flow system for the continuous monitoring thanks to their robustness [1], and in the same time their low cost makes them suitable for "in situ" and disposable uses [2].

In view of this, the first and critical step for sensors and biosensors productions is the solubilization of the modifying agent in order to obtain a stable and homogenous dispersion that usually will result in a homogenous film on the working electrode surfaces. The hydrophobicity of pristine carbon nanomaterials in most solvents, in particular in water, has limited their direct integration with biological elements and their application in biosensors designing. The overcoming of this disadvantage is necessary, taking in account the unquestioned capabilities of these nanomaterial to improve the electrochemical performances [3].

In this work, a biocompatible dispersion of pristine carbon black nanoparticle (CBNPs) is investigated. It is based on non-covalent association of CBNPs with chains of chitosan (Chit) in aqueous solutions. Among the bio-polymers the Chitosan displays excellent film-forming ability, high water permeability, good adhesion, and susceptibility to chemical modifications due to the presence of reactive amino and hydroxyl functional groups.

The homogenous dispersions of CBNPs/Chit were prepared in a range between 1-20 mg/ml and the SPEs were modified varying the volume dropped on to SPEs. The electrochemical performances of CBNPs/Chit-SPE were investigated and compared with the unmodified SPEs (Bare-SPEs) using cyclic voltammetry (CV) in presence of ferro/ferri (cyanide) as electrochemical probe.

A Significant enhancement of the electrochemical response towards several analytes such as thiocholine, cysteamine, hydroquinone and caffeic acid was observed using CBNPs/Chit-SPEs. Moreover, thanks to the compatibility of bio-



elements with Chitosan, some enzymes (such as Laccase, Peroxidase, Acetylcholinesterase) were tested incorporating them with CBNPs/Chit dispersion directly on the working electrode surface of SPEs, obtaining CBNPs/Chit/Enzyme-SPEs. Voltammetric and amperometric analysis showed the suitability of the CBNPs/Chit-SPEs as Scaffold for enzyme-based biosensors.

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## CONTROLLING DNA-BASED REACTIONS AND NANODEVICES USING ENZYMATIC REACTIONS

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DNA nanodevices or nanomachines are generally based on a conformational change activated by different kind of input: environmental changes (temperature or pH), nucleic-acids, small molecules and proteins recognized by a specific DNA sequence, or DNA-recognizing enzymes [1]. This class of possible input remains limited, so in this work we propose to expand this class using enzymes that do not recognize DNA like its specific substrate, but recognizing a small molecule, they can activate or inhibit a DNA-nanomachines. To do this we employed three different pH-dependent systems: a conformational-changing nanoswitch, a ligand-releasing nanomachine and a DNA-based strand displacement reaction, together with several classes of enzymes: a transferase, the Glutathione transferase and two hydrolases, the Urease and the Acetylcholinesterase. The glutathione transferase is a protons-producing enzyme and it recognizes its specific substrate, glutathione, in the presence of its co-substrate, 1-chloro-2,4-dinitrobenzene. Using this reaction we can finely modulate the closing of a conformational-changing nanoswitch. Instead, exploiting the reaction of the Urease with its substrate urea, that can consume protons, we can gradually open the same nanoswitch. With the second system: the ligand-releasing nanomachine we used Acetylcholinesterase, a hydrolase that can produce protons hydrolyzing its specific substrate, acetylthiocholine. In this system changing the concentration of the substrate we can finely modulate the release of the ligand, conversely using Urease and different concentrations of urea we can regulate the loading of the same ligand. With the last system: OH<sup>-</sup> dependent strand displacement reaction, we used the Urease reaction and the substrate urea like the input to start the displacement reaction. More specifically only when we added the substrate urea the strand displacement reaction started.

The possibility to use the substrate and the reaction of enzymes like a molecular stimuli in the field of DNA nanotechnology could open the door to many future exciting possibilities including enzyme-induced drug delivery and enzyme-triggered nanostructures assembly.

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## ENSEMBLES OF GOLD NANOWIRES AS SENSORS FOR TRACE ARSENIC DETERMINATION IN WATER AND FOODSTUFF

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Inorganic arsenic, that consists of both As(III) and As(V) species, constitutes the highest toxicological risk associated with arsenic in water and food in contrast to the organic arsenic species. Different analytical methods have been proposed in the literature to provide an efficient risk assessments of inorganic arsenic contamination. However there is still a clear need for more sensitive and portable sensors for easy measurement in situ. Electrochemical methods are the forefront of the research to this aim.

In this communication a study on the determination of trace levels of arsenic with gold nanoelectrode ensembles (NEEs) is presented [1]. The NEEs are prepared by electroless plating of Au nanoelectrode elements within the pores of a microporous polycarbonate template membrane. Trace concentrations of As(III) are determined by anodic stripping square wave voltammetry (AS-SWV). The square wave voltammograms recorded at NEEs are characterized by a sharp reoxidation peak at around 0 V vs Ag/AgCl sat. The method presents a detection limit of 5 ng/L after 3 min preconcentration at -0.4 V, with a linear range of 0.2 - 6 µg/L. As(V) can be determined by difference between As(III) and total inorganic As, after reduction of As(V) with cysteine. The possible interference of copper is evaluated. The method was validated with certified water sample.

The possibility to analyze inorganic arsenic in food samples, where the main fraction of arsenic compounds is organic is investigated.

Application of NEEs to trace As analysis in water and food samples, such as rice, rice cakes and seafood, and in certified material, is presented and discussed. The results are compared with those obtained by HPLC-ICP-MS [2].

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## NANOSTRUCTURED PRESS TRANSFERRED ELECTRODE COUPLED TO MICROFLUIDIC ELECTROPHORESIS, FOR PESTICIDE DETECTION

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A rapid and quantitative multi-residual screening method, for the separation and detection of carbamate pesticides in food samples has been developed. The novelty of this work is the realization of a simple method for the fabrication of electrodes based on carbon black (CB) using press-transfer technique. For the first time the press-transfer (PT) technique[1,2] was used with the nanostructured CB, that act as exclusive electrochemical transducers. The production of a stable CB nano-dispersion does not require sophisticated procedures; due to this reason combined with the low cost of the material, in recent years the use of CB as a nanomaterial has found an increasing application in electrochemical sensing [3]. CB dispersion was filtered through a PTFE membrane and press-transferred on polymethyl methacrylate (PMMA) substrates thus being readily applicable to microchip platforms. In fact, in order to make possible the separation of the analytes, the electrodes have been designed to be coupled to microchip electrophoresis device. The optical and electrochemical characterization was performed both off-chip and on-chip. The obtained material resulted physically and chemically homogeneous.

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## SIMPLE PENCIL-DRAWN PAPER-BASED DEVICE FOR ONE-SPOT ELECTROCHEMICAL DETECTION OF ELECTROACTIVE SPECIES IN OIL SAMPLES

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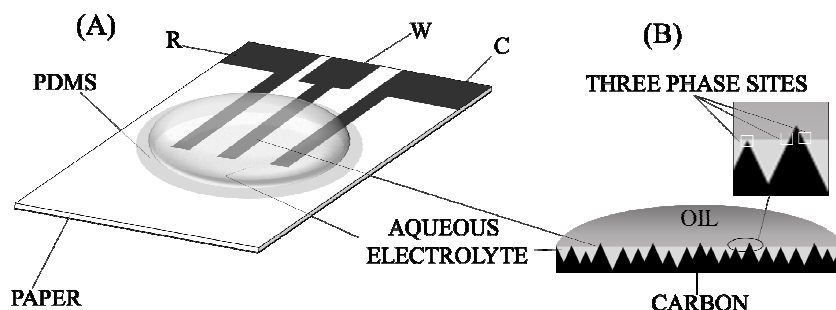
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The use of a pencil-drawn paper-based device (PDE-PED) for conducting one-spot direct electrochemical tests on vegetable oils, is proposed.

It consists of a circular cell of hydrophilic paper surrounded by polydimethylsiloxane (PDMS) hydrophobic barriers, printed by using custom-designed stamps, where working, reference and counter electrodes are drawn by in-house made pencil leads. This cell was firstly wicked with a small volume of aqueous electrolyte and then a controlled volume of edible oil samples was applied on top of the paper-based electrochemical cell to perform voltammetric measurements.

Voltammetric profiles for electroactive both hydrophobic components (e.g.  $\alpha$ -tocopherol) and water soluble species (ortho-diphenols, as well as some monophenols and polyphenols, most of them exclusively present in olive oils) were recorded. In fact, the device, is able to act as three-electrode support for detecting both hydrophobic and hydrophilic analytes at the oil/water interphase and, at the same time, as substrate for thin-film aqueous extraction and subsequent electrochemical analysis of sole hydrophilic compounds.

The whole of these results points out that olive oils display voltammetric profiles quite different from those exhibited by seed oils, thus suggesting that simple one-spot tests can be conveniently conducted at PDE-PED for the rapid and effective discrimination of edible oils.



## **A DEEP EUTECTIC SOLVENT-BASED AMPEROMETRIC SENSOR FOR THE DETECTION OF LOW OXYGEN CONTENTS IN GASEOUS ATMOSPHERES**

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Oxygen monitoring in gaseous phase is a quite widespread operation in several industrial processes and food technological applications, since it is a strong oxidizing agent able to promote a large number of undesired processes. In particular, continuous detection and control of reduced oxygen concentrations (2-6 % v/v) usually present in modified atmospheres used for preserving food is required throughout the entire packaging process. In fact, such a low oxygen content, frequently accompanied by cold storage, enables microbial growth to be reduced, as well as respiration processes of living tissues present in food to be slackened, thus allowing the relevant shelf life to be lengthened markedly. Consequently, the availability of simple, inexpensive and rapid methods for O<sub>2</sub> determination in quite wide concentration and temperature ranges is highly desirable. Among electroanalytical methods remarkable benefits are gained from the use of amperometric sensors based on room temperature ionic liquids (RTILs). Recently, a novel class of ionic liquids, named deep eutectic solvents (DESs), has been developed. They consist of eutectic mixtures of quaternary ammonium salts and hydrogen bond donors, such as alcohols, amides or carboxylic acids, displaying melting points quite lower than those proper for each component. These eutectic mixtures share with RTILs many profitable properties and, what's more, they are biodegradable, low cost and insensitive to water.

With the aim of verifying the possibility of using DESs, instead of RTILs, in membrane-free electrochemical gas sensors, we have assayed the performance of an O<sub>2</sub> amperometric sensor designed for its selective detection in food packaging processes employing modified atmospheres with poor oxygen contents. We report here the results found by such a sensor, prepared by using ethaline (eutectic formed by mixing choline chloride with ethylene glycol in the molar ratio 1:2) as prototype of DESs, in the temperature range from 2 °C (cold storage) to 26.5 °C (room temperature).

**5-PHENYL-DIPYRROMETHANE AND 5-(4-PYRIDYL)-DIPYRROMETHANE AS MODULAR BUILDING BLOCKS FOR BIO-INSPIRED CONDUCTIVE MOLECULARLY IMPRINTED POLYMER (cMIP).**

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The preparation of (molecular imprinted polymer) MIP requires that a polymer is formed around a template (the target analyte) which, reversibly embedded in the polymer network, draws a cavity defined by size and stereochemical configuration. Once the template molecule is removed, the cavity acts as a 3D recognition unit highly specific for the target analyte. In the present work the electrochemical behaviour of the 5-phenyl-dipyrromethane (**5-ph-DP**) and 5-(4-pyridyl)-dipyrromethane (**5-py-DP**) is investigated with the aim of checking whether dipyrromethanes can be useful monomers to synthesize electrochemically conductive MIP (cMIP). The interest in these molecules lies in the fact that the recognition unit is located in a remote position with respect to the two pyrrolic units, which act as polymerization sites. Further, the modular synthesis of dipyrromethanes allows the most convenient functionality for the chemical interaction with the template to easily be introduced at C<sub>5</sub> position. The proposed investigation is a proof of concept that aims first to demonstrate the role of the substituent in 5 both on dipyrromethane polymerization ability and on the recognition of the template. Then, the **5-ph-DP** and **5-py-DP** co-polymerization ability is also tested with the goal to prepare multifunctional pockets where the phenyl and pyridyl pendant groups, are acting as interactions point for the template inclusion to tune the analyte inclusion. To test the functionality of the obtained conductive homopolymers (cMIP) and copolymers (co-cMIP), salicylic acid (SA), an electroactive phenol derivative, was chosen as template prototype. The dynamic response of co-cMIP modified sensor toward SA was in a range of  $0.5 \cdot 10^{-7}$  to  $1 \cdot 10^{-6}$  M with a good selectivity respect to three interferences such as phenol, 3-hydroxy-benzoic acid and benzoic acid. The MIP sensors were tested on the extracts of willow buds.

## **ELECTROCHEMICAL BIOSENSOR FOR THE DETECTION OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN FOOD SAMPLES**

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Polybrominated diphenyl ethers (PBDEs) are persistent environmental substances that have been commonly used as fire retardants in huge number of commercial products. Their ubiquity, due to their low reactivity, high hydrophobicity and bioaccumulative properties, causes a continuous exposure to these compounds. Even if any maximum limit for PBDEs has still not defined, in March 2014 the European Commission issued a Recommendation in which member states are requested to monitor brominated flame retardants in food, in order to evaluate human and wildlife exposure. Gas-chromatographic techniques, coupled with mass spectroscopy are currently used to achieve PBDEs detection in food and environmental matrices [1]. Nevertheless, despite the high sensitivity, these methods requires complex, expensive and time consuming sample pre-treatment and analysis. For this reason there is an increasing interest in developing reliable, rapid and cheaper analytical approaches [2]. The objective of this study was to exploit the use of an electrochemical magnetic particle enzyme-linked immunoassay (ELISA) to analyze PBDEs in food samples. The immunological reaction was based on a direct competitive scheme, using an alkaline phosphatase (AP) labeled congener as tracer. After the immunological event, the anti-PBDEs antibody modified magnetic particles were captured on the surface of graphite disposable sensors. The reaction extent was finally electrochemically measured upon the addition of a proper substrate, using Differential Pulse Voltammetry (DPV). Under the optimized conditions, the electrochemical immunosensor shows a linear detection range from 0.2 to 20 µg/mL of PBDE-47 with an IC<sub>50</sub> of about 1.7 µg/mL. The assay was rapid and can be used to analyse samples in 1 h after clean up. The protocol was then coupled with QuEChERS- like extraction and SPE purification for the samples, in particular mussels. Some results were herewith presented.

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## SYNTHESIS AND CHARACTERIZATION OF HYBRID Cu/Ag NANOPARTICLES BY LASER ABLATION IN LIQUID

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Bi-metal nanoparticles (NPs) offer unique catalytic, electrochemical and optical properties, compared to mono-metal NPs [1-2]. Moreover, the case of Cu/Ag hybrid structures is particularly appealing, due to the combination of the antimicrobial activity of both metals. Among methods for preparing bi-metal NPs, laser ablation synthesis in aqueous media [3] is a relatively simple, rapid and green approach, which allows obtaining NPs of different size and shape. In previous works, we focused on the synthesis of copper nanoantimicrobials by femtosecond laser ablation of a copper target using a biopolymer as stabilizing agent (Chitosan, CS) in 0.1%<sub>v/v</sub> Acetic Acid (HAc) aqueous solution [4]. Starting from these results, here we present the preparation of Cu/Ag bimetallic NPs by a two-step laser ablation method. An original experimental setup was developed, implementing a novel flow cell system, which removes the as-synthesized colloidal particles, thus reducing their interactions with incident laser pulses. The experiments were performed using femtosecond fiber laser, operated at 1030 nm. Silver and copper targets were alternatively selected as first ablated material, followed by the ablation of the second metal, always using CS as ultimate capping agent at its optimal working concentration of 1 g/L in 0.1%<sub>v/v</sub> HAc solution, employed as liquid carrier.

Mono- and bi-metal NPs were characterized by Transmission Electron Microscopy, UV-VIS, X-ray Photoelectron Spectroscopy and diffraction techniques, to evaluate their structure, morphology and chemical composition.

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**STUDY OF THE INTERACTION BETWEEN COLLAGEN AND NATURALIZED AND COMMERCIAL DYES VIA FOURIER TRANSFORM INFRARED SPECTROSCOPY**

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We recently synthesized naturalized dyes (NDs) which are a new class of environmental friendly chemicals. ND can be obtained the covalent union of a dye species (e.g., azo, anthraquinone, aniline type chromophore) with lactose, a natural sugar. In the present work NDs and the traditional acid dyes (ADs) were compared by studying the different behavior during the leather dyeing process. NDs are able to confer water-soluble properties to the dye molecule as a whole. The interactions between the dyes and the leather proteins were studied by FT-IR spectroscopy and thermogravimetric (TG) analyses. The protein cross-linking of the dyed leather samples was investigated by studying the 1654/1690  $\text{cm}^{-1}$  peak height ratio and a deconvolution procedure of the amide I peak. The helix secondary structure was the predominant component of the leather proteins of the samples dyed with low concentrations of NDs (2%), while the  $\beta$ -sheets prevailed when leather samples were dyed with the traditional ADs and high concentrations of NDs (>5%). The data were discussed with respect to TG results

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D. Pellegrini, M. Corsi, M. Bonanni, R. Bianchini, A. D'Ulivo, E. Bramanti, *Dyes and Pigments*, 116, 65-73 (2015)

## PHOTOCHEMICAL VAPOR GENERATION OF SELENIUM(IV) AND ARSENIC(III) WITH COMMERCIAL AND HOMEMADE UV LAMPS

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Nowadays photochemical vapor generation (photo-CVG) is a good competitor of conventional chemical vapor generation for the determination of hydride-forming elements, transition metals and non-metals. Photo-CVG is based on the absorption of ultraviolet (UV) radiation by a low molecular weight organic acid, which generates radicals necessary to the vapor generation process [1].

Our study is focused on the photo-CVG with formic and acetic acid of Se(IV) and As(III) inorganic species. For Se(IV), we used a commercial mercury-UV germicidal lamp with formic acid at low concentrations and we obtained yields comparable to those of the classic CVG methods. Photo-CVG of As(III) was much less efficient and the yield was at least 10 times lower than Se(IV), but with quite similar trends varying the organic acid concentrations [2].

This work was also aimed to extend the operating range of the photo-CVG from usual electroded lamps to mercury microwave-electrodeless discharge lamps (MW-EDL). To the best of our knowledge, this type of UV lamps has been employed for organic matter pre-digestion process [3], and for the photo-CVG of Hg for trace analysis [4]. Here we report for first time the generation of volatile hydrides by using photo-CVG with MW-EDL for trace analysis. Data collected from mercury-MW/UV photo-CVG analysis have shown behaviors similar to those obtained for the classical UV discharge lamps for both inorganic As and Se species. The Photo-CVG yields varied with microwave generator power. Photo-CVG experiments made with classic mercury lamp (emission spectral line at 254 nm) were compared to those performed with a homemade cadmium MW-EDL lamp (emission spectral line at 228 nm). The preliminary results seemed to confirm the possibility of using, for the photochemical vapor generation, spectral emission lines different from those achievable by the use of mercury lamp.

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## **IN VITRO SELECTION OF RNA APTAMER AGAINST CA125 TUMOR MARKER IN OVARIAN CANCER AND ITS STUDY BY OPTICAL BIOSENSING**

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Early identification of neoplastic diseases is essential to achieve timely therapeutic interventions and to significantly reduce the mortality of patients. The Cancer Antigen 125 (CA125) or mucin 16 (MUC16), a glycoprotein of the human family of mucins, already used for the diagnostic and prognostic evaluation of ovarian cancer is a well-known biomarker and its detection remains a promising tool in the early diagnosis of this tumor. Development of new methods for the detection of this biomarker could be an interesting starting point in the direction of coupling these receptors to emerging analytical platforms with application to clinical diagnostics.

With this aim in mind, the development by SELEX of nuclease-resistant RNA aptamers able to bind with high affinity the CA125 antigen as purified protein is here reported. The selection method involves His tag biomarker conjugation on Ni-NTA agarose magnetic beads. The binding kinetics of selected aptamers were determined by Surface Plasmon Resonance (SPR) technology (Biacore X). To achieve significant binding by SPR technique, a dedicated protocol was suitably developed. Two different CA125 immobilization strategies were evaluated, the first one employing NTA chips achieving immobilization via His tag tail, and the second one employing CM5 dextran chips for covalent protein immobilization. Moreover, assay conditions were optimized in terms of binding buffer. Calibration and affinity constants for the selected aptamers were finally reported, leading to possible future clinical applications of this new method for the detection of the Cancer Antigen 125 (CA125).

**DETERMINATION OF REY, Zr AND Hf IN HIGH ARSENIC CONTENT MATRIX. A CASE STUDY AT THE SOLFATARA OF PHLEGREAN FIELDS (NAPLES, ITALY)**

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The sublimation process is associated with active volcanism and takes place through a very fast cooling of a gas released from a fumarolic vent. Sharp temperature and compositional changes in the volcanic gas phase, when it encounters the atmosphere, cause the deposition of authigenic solids (hereafter defined sublimates) in fumaroles.

There is a lack of knowledge regarding the Zr, Hf and REY (lanthanides plus Y) fate at the sublimate-volcanic gas interface, which could provide information about the transport of these elements in the volcanic gas phase. With the aim to establish the mutual behaviour of Zr, Hf and REY during the transport in volcanic fluids, as part of our project in different volcanic systems, we have studied the products of sublimation of the fumaroles at the Solfatara of the Phlegrean Fields (Naples, Italy). Sublimates were collected from the inner walls of silica tubes (1.5 m long) positioned within the fumarolic vent [1]. However, high concentrations of As (up to 82 g/kg) were measured in the samples collected (essentially As<sub>2</sub>S<sub>3</sub> and minor amounts of other sulphides) and these high amounts made more difficult the correct determination of Zr, Hf and REY. To “clean” these samples were used selective and/or coprecipitation methods but without good recovery. Therefore, to determine the REY, Zr and Hf amounts, the samples were treated adapting, for comparison purposes, two different classical treatments. In the first, sample aliquot was dissolved in concentrated NH<sub>3</sub> to bring into solution only As<sub>2</sub>S<sub>3</sub>. Subsequently, the filtered undissolved residue was dissolved in concentrated HNO<sub>3</sub>. In the second treatment, sample aliquot was treated with HCl 8M to dissolve all the sulphide present with the exception of As<sub>2</sub>S<sub>3</sub>. Both of the resulting solutions were analyzed by Q-ICP-MS. The method was validate in terms of linearity, sensitivity, precision, and recovery while the accuracy was tested by the standard addition procedure.

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## XPS AND FTIR SPECTROSCOPY CHARACTERIZATION OF PHOTOTROPHIC BACTERIAL CELLS INTERACTING WITH NICKEL IONS

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The intensification of industrial technology increased heavy metal contamination in aquatic systems. Since inorganic pollutants cannot be degraded, an efficient removal system must be designed in order to detoxify heavy metal-contaminated wastewaters. Metal ion biosorption by microorganisms is an interesting mechanism which can be exploited for this purpose. The purple bacterium *Rhodobacter sphaeroides* is known for its ability to tolerate under phototrophic conditions high concentrations of several heavy metal ions and to bioaccumulate Ni<sup>2+</sup> and Co<sup>2+</sup> ions [1].

In this work Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy and X-Ray Photoelectron Spectroscopy (XPS) have been employed for getting information about Ni<sup>2+</sup> binding onto *R. sphaeroides* cell surface. The ability to bind nickel ions was evaluated both in free cells and in calcium alginate-immobilized biomass. Before Ni<sup>2+</sup> exposure the bacterial biomass was washed thoroughly with KCl 0.1 M in order to fully saturate with K<sup>+</sup> ions the negatively charged cell envelopes. XPS measurements revealed that treatment with Ni<sup>2+</sup> resulted in full displacement of K<sup>+</sup> ions from free *R. sphaeroides* cells, indicating high affinity between nickel ions and surface functional groups. Moreover ATR-FTIR measurements showed that Ni<sup>2+</sup> treatment induce the shift of absorption bands arising from symmetric and asymmetric stretching modes of cell surface carboxylate groups, in agreement with their involvement in metal complexation. These data are of interest in order to identify optimal conditions for the efficient removal of Ni<sup>2+</sup> by means of phototrophic bacterial biomass.

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**ANALYTICAL CHARACTERIZATION OF SILVER-NANOPARTICLE ANTIMICROBIAL COATINGS FOR FIORDILATTE CHEESE**

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Recently, the interest in antimicrobial food packaging has increased considerably because of the potential use of an active system for prolonging the shelf life of stored food. Data in the literature indicate that use of bio-based coating could represent an interesting strategy to allow better preservation of fresh dairy products [1]. Metallic nanoparticles are promising because they show improved antibacterial properties due to their large surface area to volume ratio. Silver nanoparticles have been receiving considerable attention because of their attractive physicochemical properties and strong toxicity against a wide range of microorganisms [2]. They have also strong inhibitory and bactericidal effects [3], so they are potential candidates for active packaging. In fact, silver nanoparticle coatings have shown to exert a marked inhibitory effect on the growth of microorganisms, and so they are used in many daily life materials. In this work, active calcium-alginate coatings loaded with silver-nanoparticles, have been characterized by XPS and ATR-FTIR. These coatings have already shown to be effective in prolonging shelf-life of fiordilatte cheese as recently reported [4]. An appreciable silver amount has been detected on the film surface. Furthermore, ATR-FTIR confirms the presence of silver nanoparticles and their interactions with alginate. SEM was also carried out in order to investigate the distribution and morphology of silver nanoparticles.

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## **XPS CHARACTERIZATION OF PDMS BASED MICROFLUIDIC CHANNELS OF CLINICAL APPLICATION TREATED WITH DIFFERENT SOLVENTS**

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Poly(dimethylsiloxane) (PDMS) is widely used in microfluidics due to its ease of use and patterning in designing and fabricating devices components by soft-lithography, low cost, optical transparency, elasticity, tunable wettability and permeability to gases as well as biocompatibility [1-3].

Among appealing properties, PDMS exhibits low chemical resistance as a major disadvantage. In fact, it swells in presence of common organic polar solvents and concentrated acid solutions. Such limited compatibility between PDMS and solvents/solutions is critical because it can involve severe practical limits in terms of channel deformation/collapse and loss of active solute while employing PDMS channels with cancer and disease tracers [4,5]. In this study, we investigate the surface modifications of PDMS in presence of organic solvents and aqueous solutions. In detail, X-ray Photoelectron spectroscopy analyses illustrate the surface chemistry of PDMS sample treated with dichloromethane (DCM), iodidric acid (HI) and an aqueous solution of fluorodeoxyglucose (isotopically labelled FDG). This solution is of very interest because of its effective sensitive tumor detection via positron-emission therapy (PET) imaging.

Optical observations under visible and UV light were also carried out in order to evidence surface morphological changes induced by the PDMS solvent contact.

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## **CONTAMINATION BY ORGANOTIN COMPOUNDS IN THE GULF OF LA SPEZIA AFTER THE INTERNATIONAL BAN OF TBT IN ANTIFOULING PAINTS**

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Organotin contamination in the aquatic environment is of global concern; tributyltins and triphenyltins are toxic to aquatic life and are used worldwide not only as biocides in antifouling paints but also as preserving agents for wood and timber, and as agricultural fungicides.

Formulations containing tributyltin, (TBT) were the most successful compounds against biofouling and were extensively used on 70% of the world's fleet. Unfortunately, TBT exhibited detrimental impacts on sea life, causing for example imposex, i.e. the development of male characteristics in female gastropods. [1]

Therefore, since the 1980s some European countries introduced restrictions on using TBT-based paints and an ultimate global ban by IMO (International Maritime Organization) for all vessels was enforced in 2008.

With this work we have tried, wherever possible, to check the status of contamination by organotin compounds in the La Spezia Gulf after the ban enforced by IMO. The analysis have been carried out on seawater, sediments and mussels by analytical methods developed in ENEA laboratories. The results of two sampling campaign (winter and summer) have been compared with data obtained in 1990 in the same sea area [2].

The results for the seawater have shown the presence of TBT in samples taken close to La Spezia port (unit ng/L as (Sn)). The data on marine sediments have shown the same picture, where the presence of organotin compounds is higher in the sampling points close to port (tens  $\mu\text{g/Kg}$  as (Sn)). Concerning the mussels analysis, quite high concentrations of TBT (tens  $\mu\text{g/Kg}$  as (Sn)) have been found in two sampling sites, which may be justified with their proximity to areas where the sediments are more contaminated. Indeed, the contaminated sediment may continue to act as input sources of TBT to overlying water by desorption or resuspension of sediment-bound TBT in areas where maritime traffic is high. The comparison with 1990s campaign has shown a clear and strong decrease in organotin concentration in the Gulf and that the presence of contamination is not due to recent input of TBT in seawater.

TBT is identified as priority hazardous substance in the Water Framework Directive and if we compare the TBT monitoring data obtained in this work with the maximum allowable concentration of 0.6 ng/L as Sn, we can conclude that this kind of contamination is still an environmental issue.

TBT will probably cause problems long after it has been banned, remaining a matter of concern and requiring monitoring for years to come.

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**MAGNETIC AND HIGHLY REUSABLE MACROPOROUS SUPERHYDROPHOBIC/SUPEROLEOPHILIC PDMS/MWNTS NANOCOMPOSITE FOR OILS SORPTION FROM WATER**

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Oil/water separation is a worldwide challenge to prevent serious environmental pollution. Development of sorbent materials with high selectivity, sorption capacity, easy collection and recyclability is required for spilled oil recovery. In this field, sorbent magnetic controllable materials have received broad attention due to the possibility of easily being driven to polluted area and recovered by simple magnetic interaction [1]. However most of them need a complex and expensive synthesis and exhibit low reusability, low oil uptake ability and low mechanical properties [1,2].

We propose for the first time a 3D sponge made of porous polydimethylsiloxane (PDMS) embedding magnetic multi-walled carbon nanotubes (MWNTs) fabricated by polymerizing PDMS in the presence of a hard template covered with magnetic MWNTs. The proposed fabrication technique is simple, low cost and easy to be scaled up. The presence of MWNTs in polymer matrices, not only provides magnetic properties to the sponges, but has also a great impact in improving their mechanical properties, thermal stability and oil uptake ability. The material can selectively collect oil from water reaching the equilibrium in less than two minutes evidencing a high volume sorption capacity (between 3 and 5 cm<sup>3</sup>/cm<sup>3</sup>). The sponges exhibit excellent mechanical performance with respect to other proposed oil-uptake systems maintaining their characteristics after 50 cycles at 90% strain. Their superhydrophobicity/superoleophilicity, allowing two times faster oil sorption with respect to other PDMS based porous materials, along with high thermal and chemical stability, makes them very attractive as high-performance systems for plugging oil leakage.

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**QUANTIFICATION OF INDOLE-3-ACETIC ACID, BENZOIC ACID AND SALICYLIC ACID IN PLANT EXTRACTS BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY**

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Phytohormones are a family of plants secondary metabolites, and their accurate determination is fundamental to understand the effects of abiotic and biotic stress on plant growth and development.[1]

Here we propose the determination of three major plant metabolites, indole-3-acetic acid, benzoic acid and salicylic acid by gas chromatography mass spectrometry (GC – MS). Before the analysis the analytes were converted into the respective ethyl-ester by single-step aqueous derivatization with triethyloxonium tetrafluoroborate. Compared to common derivatization approaches for GC analysis, the proposed method has the advantage to be based on a simple aqueous chemistry.

Optimization of some effective parameters for the derivatization step – such as pH of the reaction medium, amount of reagent, and derivatization/extraction time – was established.

Phytohormones were simultaneously extracted and derivatized from *Nicotiana tabacum* and *Actinidia deliciosa* samples. The sample preparation involves only centrifugation, aqueous derivatization and liquid-liquid extraction of the resulting ethyl-esters with MTBE. Linearity, repeatability, recovery, limit of detection and quantitation were evaluated for each analyte under investigation, along with the matrix effects. The results were compared to those obtained by analyzing the derivatized extracts by liquid chromatography coupled to diode array/fluorescence detector.

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**MONITORING OF MERCURY IN THE ITALIAN DOLOMITES.**

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A monitoring station for Total Gaseous Mercury (TGM) has been installed at Col Margherita in the Dolomites in the Province of Belluno. Its location on the southern side of the Alps is unique, making it the ideal site for the evaluation of emissions from the Po Valley, one of the largest industrial areas in Europe.

The climate is cold with heavy snowfall in winter, making it a potential pilot site for the study of the mechanisms of cold-trapping of volatile and semi-volatile inorganic pollutants such as mercury.

Preliminary results for air monitoring cover November 2012 to present, wet deposition fluxes of total mercury (THg) were determined from January 2014 to January 2015. Event-based precipitation samples were collected according to mercury standard operative procedure (SOP) shared between all partners in the Global Mercury Observation System (GMOS) project [1]. Each sample was analysed by cold vapor atomic fluorescence spectrometry (CVAFS) following European standard and EPA methods [2, 3]. The total Hg (THg) concentrations and fluxes ranged from 1.4 - 44.1 ng/L for the respective June and November samples. The volume-weighted mean concentration (VWM) and the annual wet deposition fluxes of THg were estimated as between 7.8 ng·L<sup>-1</sup> and 4.4 µg·m<sup>-2</sup>·yr<sup>-1</sup> during the study period.

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## **ANALYSIS OF WC-Co NANOPARTICLES IN SLUDGE FROM A SEWAGE TREATMENT PLANT**

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In the last decades the use of nanotechnology is rapidly increased in many sectors including agriculture and food industries, medicine and healthcare, energy, material, electronic, construction and chemicals industries and a considerable number of products containing nanomaterials is available on the market. Actually the potential risks related to their production, use and disposal are not completely known and some impacts are expected on the environment throughout the nanomaterial life cycle. In particular, nanomaterials might negatively interfere in various water and wastewater treatment processes [1], and suitable characterization methods are needed to understand their behavior and fate in the sewage treatment plants.

This work focuses on the detection of WC-Co nanoparticles, a hard composite metal produced by a top-down approach commonly used to coat cutting tools and with a well-known toxicity [2], in sludge derived from a sewage treatment plant.

After characterization of the pristine WC-Co nanoparticles to assess their size, size distribution, surface area and stability in water, different digestion methods have been compared to quantify W and Co concentration by ICP-MS in sludge and soil/sludge mixture: two methods on hot plate under relatively mild digestion conditions [3, 4] and a microwave assisted acid digestion employing hydrofluoric acid. This latter method produced the best performances in terms of recovery (W= 113 % and Co= 95 % with respect to a known spiked concentration) and repeatability (W= 7 % and Co= 10 % measured as standard deviation of 8 replicates), although the presence of a black non-digested matter at the end of the mineralization, so it was applied to sludge samples for the risk analysis of WC-Co nanoparticles on the biological function of sewage treatment plants.

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## **ANALYSIS AND DETECTION OF DIURON IN SEAWATER BY PASSIVE SAMPLING**

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Colonisation by fouling organisms is a problem for any structure placed in the aquatic environment and can be controlled through both chemical biocides and non-biocidal technologies. Up to now the majority of vessel hulls are protected by antifouling (AF) paints containing biocides. Organotin biocides, especially tributyltin (TBT) compounds, have historically been used extensively as effective antifouling agents, but due to the detrimental effects towards various marine organisms, the International Maritime Organization (IMO) banned worldwide the use of TBT and similar compounds (IMO 2001) since 2003.

Consequently, paint manufactures have developed new tin-free formulations made of a main active component and additional biocide. Diuron was reported as the most common biocides in coastal waters and seems to be extremely resistant to degradation in seawater. The compound exerts its antifouling action by inhibiting photosynthesis and impairing electron transport within chloroplasts. Hence, it seems to have potential toxic effects on several aquatic non-target species among primary producers [1]. Therefore diuron needs to be monitored in order to assess the possible environmental damage related to their use.

Monitoring by passive sampling (PS) has proven to be a scientifically sound and economic alternative to grab water sampling [2]. PS devices are usually based on diffusion through a well-defined diffusion barrier or on permeation through a membrane. Several designs of passive samplers have been proposed, where the main characteristic is the collecting medium utilized in the system. The so-called POCIS device comprises a solid receiving phase material (non-polar sorbent), sandwiched between two microporous polyethersulphone diffusion-limiting membranes. These passive samplers are used to sample hydrophilic compounds with octanol/water partition coefficients  $\log_{KOW} < 3$  (polar organic pollutants, drug residues, pesticides, etc...).

The aim of this study is to assess the performance of POCIS passive sampling for the analysis of diuron in seawater with a critical evaluation of the analytical method of detection and quantification.

For diuron extraction and analysis from POCIS, two chromatographic methods of detection have been studied, GC-MS and HPLC/UV. One of the differences between GC and HPLC methods is that in GC diuron is analysed as its isocyanate, i.e. the diuron degradation product formed during hot GC injection.

The results of the study were assessed to obtain a fast though efficient and sensitive method of determination able to comply with the Environmental Quality Standards (EQS) established for diuron in the Water Framework Directive.

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**SPATIAL AND TEMPORAL VARIABILITY OF SNOW CHEMICAL COMPOSITION AND ACCUMULATION RATE AT TALOS DOME SITE (EAST ANTARCTICA)**

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Five snow pits and five firn cores were sampled during the 2003/04 Italian Antarctic Campaign at Talos Dome (East Antarctica), and analysed in order to study the spatial and temporal variability of chemical markers and annual snow accumulation rate at this site.

All the samples were analyzed by two conductivity-suppressed Ion Chromatographs, for anion ( $F^-$ ,  $MS^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ) and cation ( $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ) determination.

Thanks to the marked seasonal pattern of selected parameters, it was possible to accomplish an accurate dating of the firn cores and snow pits.

In order to achieve an overview of the average chemical composition and load of particular ion species in snow layers at Talos Dome, an ion balance was calculated from average value of each component in each stratigraphic record. All the snow pits showed an evident and quite reproducible acidic character, with primary ( $Na^+$ ,  $Cl^-$ , partially  $SO_4^{2-}$ ) and secondary ( $SO_4^{2-}$ , MSA) marine sources, together with nitrate/nitric acid as the major contributors to the chemical composition. The total ionic load is larger during the summer period, as well the free acidity, exhibiting values between the 35% and 65%, against 16%-45% observed in winter.

The different snow pits and cores showed a small variability of the median values of sea salt components ( $Na^+$ ,  $Cl^-$  and  $Mg^{2+}$ ) and also  $Ca^{2+}$ ,  $K^+$ ,  $F^-$ ,  $NO_3^-$  and  $SO_4^{2-}$ . As concerning  $MS^-$ , it showed higher values in snow pits than in firn cores, very likely due to diffusion processes leading it to move from the inner to the external part of ice cores.

As concerning the study of the accumulation rate variability at Talos Dome, average values were found in the range 70.3-85.4 mm w.e. (water equivalent)  $yr^{-1}$ , and small differences from one point to another (e.g. 70 and 74 mm w.e.  $yr^{-1}$  in the N-NE part against 92 and 81 mm w.e.  $yr^{-1}$  in the S-SW part) of the site were found and interpreted in terms of wind-driven redistribution processes and accumulation areas, as also found in previous studies.

The comparison of the different sampling points in this site confirmed the larger importance of the temporal variability rather than the spatial variability in terms of average composition and concentration of the chemical markers, supporting the reliability of Talos Dome site for paleo-environmental and paleo-climatic studies.

## **SURFACE SNOW AT DOME C: CHEMICAL COMPOSITION FROM LONG-TERM CONTINUOUS RECORDS ON THE ANTARCTIC PLATEAU**

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Antarctica is the most pristine and remote region in the world, far from pollution sources and with negligible anthropic inputs. Aerosol particles and atmospheric gases can be trapped in the snow layers by atmospheric scavenging processes, so the interpretation of chemical stratigraphies of ice cores drilled in such remote regions allows to obtain an excellent data set for paleoclimatic and environmental information.

Year-round snow samplings were carried on for several consecutive years at the inner French - Italian station Concordia in Dome C (75°06' S, 123°23' E), on a 3300 m a.s.l. plateau, in parallel with aerosol measurements. The aim of this sampling programme was to obtain information on the main natural sources, the transformation processes and the prevailing long-range transport patterns of the atmospheric particulate matter and to understand what depositional and post-depositional processes can affect some chemical markers once they are deposited from atmosphere on the snow. Dome C is the same site where EPICA (European Project for Ice Coring in Antarctica) ice core (providing about 800.000 years of paleo data) was drilled in 2004.

Sea salt Sodium (ssNa<sup>+</sup>), a snow-preserved analyte, is used as sea spray marker and its inter-annual trend, together with the study of sulfur compounds SO<sub>4</sub><sup>2-</sup> and MSA (Metansulfonic Acid), can be related to the atmospheric circulation modes affecting the oceanic areas around Antarctica; ssNa<sup>+</sup> in ice cores is a common proxy for sea ice extention.

Sulfate, Nitrate and Chloride are the main ionic components in Dome C snow. They show different seasonal trends: while Sulfate and Nitrate are characterized by summer maxima (especially Nitrate, with very sharp summer peaks), Chloride follows Sodium seasonal trend, with winter maximum concentration values. Despite common trends for Sodium and Chloride, their stoichiometric ratio is not 1:1 as in NaCl, but there's a Chloride depletion due to the general acidity of Dome C snow. This fact brings to a loss of volatile acids, such as HCl, from snow layers. Calcium (Ca<sup>2+</sup>) is a typical crustal marker that provides the background level of continental contribution (mainly from South America), from erosion and long range transport processes, to the Antarctic Plateau.

**FIVE YEARS OF AEROSOL SIZE DISTRIBUTION DURING SPRING-SUMMER CAMPAIGNS AT NY ÅLESUND (SVALBARD ISLANDS, NORWAY)**

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The Arctic is one of the most sensitive region about the climate changes: every variation in the mean temperatures is amplified in the Arctic, triggering positive feedback mechanisms. The aerosol is one of the most important forcing factors affecting the climate but its contribution on the radiative balance of the planet is still affected by a large uncertainty. The final behaviour of the particles in the interaction with the solar radiation and their tendency to form clouds, depends on their composition and dimension. In order to better understand the role of the aerosol in the polar regions and the weight of the anthropic sources, the particles size distribution was investigated during spring and summer (from March to September) since 2010. The sampling site was Ny Ålesund in the Svalbard Islands, Norway, and the measurements were carried out by two particle counters: (1) TSI SMPS, 54 channels, to detect nanometric particles between 10 and 487nm; (2) TSI APS, 52 channels in the range 0.5–20µm; both with a 10-minute resolution. Aerosol samples were simultaneously collected, in order to have a daily chemical profile of the particles, useful in the identification of the aerosol sources. In the micrometric fraction, collected by APS, we saw a low number of particles, which is mainly included in the range 0.7–1.1µm. The fine fraction distribution showed a large number of particles in the accumulation mode (0.1–0.3µm) in spring. Whereas in the late spring and during the summer, we observed many nucleation events between 0.02 and 0.05µm. The chemical analysis on the particulate, showing that the aerosol is mainly composed by sulphate in spring, could explain the presence of a great quantity of particles around 0.2µm, sign of long range sources contribution. In the five years of sampling the characteristic pattern of the Arctic site with the rapid shift from an accumulation mode dominated aerosol to an Aitken mode dominate distribution in late spring-summer is observed. Such a pattern is explained as function of chemical composition and transport pattern changes and it seems caused by a combination of several effect: change in atmospheric transport processes, enhanced wet deposition, and increased solar radiation, all of which favour homogeneous new particle formation in the atmosphere.

**METALS AND LANTHANOIDS DETERMINATION IN ATMOSPHERIC AEROSOL SAMPLES AS MARKERS OF HEAVY FUEL OIL PROCESSING SOURCES.**

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Heavy fuel oil treatment processes (including combustion, ship traffic, refinery etc.) generate, in addition to large amount of gas, metals (e.g. V, Ni) and polycyclic aromatic hydrocarbons which have a well-known hazardous effects to health. In particular, maritime transport is currently gaining relative weight with respect to air and road and the study of the contribution to this source to the atmospheric particulate is a new challenge for the atmospheric scientific community. In the Mediterranean region the simultaneous presence of elevated anthropic and natural emissions make this region one of the most polluted in the world. This multiplicity of sources (some of them having the same markers of ship aerosol) makes hard the quantification of ship aerosol in such environment. Here we present the experimental identification of aerosols emitted from ships travelling along the main Mediterranean shipping route. PM10 aerosol samples were collected during summer 2013 within the framework of the Chemistry and Aerosol Mediterranean Experiment (ChArMEx) at two sites located North (Capo Granitola, 36.6°N, 12.6°E) and South (Lampedusa Island, 35.5°N, 12.6°E), respectively, of the main ship route in the Sicily Channel. The PM10 samples were collected with 12 hour time resolution at both sites. After weighting, the aerosol samples were analysed for ions, metals and selected lanthanoid elements. Due to the low concentration of lanthanoids in these samples, an improved method by Inductively Coupled Plasma Atomic Emission Spectrometer (ICPAES, Varian 720-ES) equipped with an ultrasonic nebulizer (U5000 AT+, Cetac Technologies Inc.) was set up.

The evolution of V and Ni concentrations (typical markers of heavy fuel oil related source) was related to meteorological conditions, backward trajectories, wind intensity and direction. Refinery emissions are characterized by elevated La/Ce and La/V ratios, due to the use of La in the fluid catalytic converter systems. The combination of lanthanoids and air-mass trajectories allowed to unambiguously identifying the ship source in the Sicily channel.

**STUDY OF ATMOSPHERIC AEROSOL IN THE PROXIMITY OF A WASTE INCINERATOR PLANT IN TUSCANY**

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Montale is a small town in Tuscany characterized by high PM<sub>10</sub> levels. There are many concerns in the population and in the press about the causes of the high levels of pollution in this area, also due to the presence of a waste incinerator plant close to the town. For these reasons, the Regional Government (PATOS2.2 project) promoted an extensive field campaign for the aerosol characterization, to give to policymakers the knowledge and the tools for a reduction of the main anthropogenic emissions. In the frame of this project, particulate matter has been collected with both daily and hourly time resolution. While daily sampling allowed the study of PM for a long period (seasonal changes in aerosol composition), hourly sampling helped in disentangling the contributions from different aerosol sources due to the capability of tracking rapid changes (atmospheric transport and dilution processes). Daily PM<sub>10</sub> samples were collected for 1 year by the FAI Hydra Dual sampler simultaneously on Quartz and Teflon filters, and analyzed by different techniques in order to obtain a complete chemical speciation (elements by PIXE and ICP-MS, ions by Ion Chromatography, elemental and organic carbon by a thermo-optical instrument). Hourly fine (< 2.5 μm) and coarse (2.5-10 μm) PM samples were collected for shorter periods (both in winter and in summer) by the Streaker sampler and hourly elemental concentrations were obtained by PIXE analysis. The concentrations of PM<sub>10</sub> were lower in spring (10-20 μg/m<sup>3</sup>), with peaks in correspondence of episodes of Saharan dust transport. PM<sub>10</sub> concentration peaks in winter are due to the typical weather conditions: higher atmospheric stability, a reduced height of the boundary layer and a poor dispersion of the pollutants themselves. Positive Matrix Factorization identified 10 sources for PM<sub>10</sub>. Biomass burning was the source that gave the most important contribution to the PM<sub>10</sub> mass (31%). Incinerator source (estimated as about 5%), mostly composed by EC, OC, NO<sub>3</sub><sup>-</sup> and traced by specific elements (Cl, Pb, Cd, Zn), was present during all the campaign.

F. Lucarelli, G. Calzolari, M. Chiari, M. Giannoni, D. Mochi, S. Nava, L. Carraresi NIMB 318 (2014) 55-59.

**HIGH RESOLUTION FAST ION CHROMATOGRAPHY: RECOVERING PALEO-RECORDS FROM ANTARCTIC ICE-CORES.**

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In the last years the increasing interest on the understanding of global climatic changes and on natural processes related to climate yielded the development and improvement of new analytical systems dedicated to measurements on environmental samples. Particular attention was paid to the chemical analysis of ice samples from deep cores drilled in polar regions: indeed, snow layers deposited year after year on the Antarctic and Greenland plateau areas trap and preserve several markers able to provide information about past atmospheric composition and climatic variations.

The determination of trace chemical species is a useful tool in paleoclimatology and the techniques for the analysis of ice core have evolved during the last few years from laborious measurements on discrete samples to continuous techniques allowing higher temporal resolution, higher sensitivity and, above all, higher throughput.

A previous FIC method used for chloride, nitrate and sulphate measurement along the Dome C core has been improved to allow high resolution sulphate determination in the EPICA Dronning Maud Land (EDML) deep core. The improved FIC method has been able to yield a 1.0 cm resolution sulfate profile for the EDML core. Two IC systems are arranged in parallel and the sample coming from a melting device is loaded in turn into two pre-concentration columns by a third external valve switching every 15 seconds. While the sample is loaded in the first IC valve (load position), the second one is in the inject position and the sample is injected and then separated in the guard-column. The three valves switch simultaneously. The total time for a single analysis is just 30 seconds and the resulting sampling resolution is 1.0 cm with a typical melting rate of 4.0 cm min<sup>-1</sup>. The measured standard deviation for sulfate is lower than 5.0 % and the detection limit is 4.0 µg/l. The high resolution profile obtained by joining data from the two ICs proved to be able to show the seasonal trend of the biogenic sulphate as well as to detail volcanic horizons. Whereas the identification of volcanic events revealed to be successful even with the previous method, whose resolution was lower, the chance of detecting seasonal pattern of sulphate has been possible only using this high-resolution method. The data obtained with this novel FIC method will allow a dating of the EDML core via annual layers counting for the last 6700 years.

**DETERMINATION OF ALKYLPHENOLS IN RIVER WATER USING AN ETCHED STAINLESS STEEL WIRE - IONIC LIQUID - SOLID PHASE MICROEXTRACTION TECHNIQUE.**

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Alkylphenols (APs) are ubiquitous environmental endocrine-disrupting chemicals (EDCs) arising from the degradation of alkylphenol polyethoxylates (APnEOs) in water systems. Emerging research suggests that APs are widely distributed in various environmental matrices, and an increased awareness of their presence has led to an intensified interest in the trace analyses of these compounds [1]. In this study, an etched stainless steel wire - ionic liquid (IL) - solid phase microextraction (SPME) device was developed for the direct extraction of four APs from water samples, namely 4-n-pentylphenol (4-NPP), 4-n-hexylphenol (4-NHP), p-tert-octylphenol (P-TOP) and nonylphenol (NP). The experimental data demonstrated that the etched stainless steel wire was a suitable substrate for IL-SPME, maintaining its high mechanical strength and, at the same time, a significant adsorption power toward ILs. The coating was prepared by direct deposition of the ILs onto the surface of the etched stainless steel wire, which exhibited a porous structure and a high surface area. Among the others ILs, 1-butyl-3-methylimidazolium hexafluorophosphate ([C<sub>8</sub>MIM][PF<sub>6</sub>]) exhibited maximum efficiency under the following experimental conditions: extraction time of 30 min, pH 2, sample temperature of 40 °C, and stirring. The IL coating exhibited an enrichment factor (EF) for the four APs, defined as the ratio between the concentration of the target compounds after and before the extraction, in the range 1382 – 4779. The detection limits (LOD, S/N = 3) ranged from 0.01 to 0.04 ng mL<sup>-1</sup>, and the RSD values for purified water spiked with APs ranged from 4.0 to 11.8% (n = 3). The calibration curves were linear in the range 0.5 - 200 ng mL<sup>-1</sup> (R<sup>2</sup> > 0.95). The optimized method was successfully applied for the analysis of real water samples.

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## INFLUENCE OF ILLUMINATION ON LIPID COMPOSITION OF THE SOFT CORAL *Sinularia flexibilis*

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The soft tissue of corals is rich in lipids. The content of total lipids in corals varies with different environmental factors, in particular with light intensity and quality [1]. In this work we studied the influence of different sources of illumination on fatty acids (FAs) composition of total lipids of the soft coral species *Sinularia flexibilis* (class Ocorallia, order Alcyonaria). Several green and grey soft corals of this species were purchased from “La Casetta in Canada”, Settimo Torinese (TO), Italy. After transport from Singapore, specimens were exposed to HQI and LED lights. Coral fragments were collected at times 0, 1, 2, 7 and 30 days post arrival. Samples were homogenised and lyophilized until constant weight. Lipids were extracted by petroleum ether:acetone (2:1, v/v) using microwave extraction [2]. Methyl esters of fatty acids (FAMES) were obtained from total lipids extract adding 1% of sodium methylate/methanol [3]. GC/MS analyses were performed using a temperature-programmed mode on an Agilent-6890 gas chromatograph equipped with an Agilent-5973N quadrupole mass selective detector, column CC-wax-MS (30 m, 0.25 mm, 0.25 µm). Preliminary data show that FA profiles of the species investigated were similar to those of other representatives of the genus *Sinularia* [4]. The main FAs present in all the specimens were 16:0, 18:0, 20:4n6, 20:5n3, 16:2n7 and 18:2n9. On the average, saturated, monounsaturated and polyunsaturated FAs contributed ~54%, ~6% and ~40% of total coral FAs, respectively. Important changes in FAs composition were observed in particular in the green specimen under HQI light starting from day 2 post arrival, with a significant increase of 14:0, 16:0, 22:0, 16:1n7, 18:1n9, 18:2n6, 18:3n6, 20:3n6 and 22:6n3 and a significant reduction in 18:0, 16:2n7, 20:4n6.

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**GLOBAL WARMING: INFLUENCE OF TEMPERATURE ON LIPID COMPOSITION OF ANTARCTIC FISH *Trematomus Bernacchii***

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Raising temperatures (which on the basis of mathematical-ecological models will be in the range of 1-6.4 °C over the next 50-100 years) have a negative influence on the physiological and biogeochemical processes of organisms, not least on the lipid composition of tissues and the cellular membrane fluidity in phytoplankton, zooplankton and fish [1].

In this work, we studied the effect of warming on the lipid composition of *Trematomus Bernacchii*, a nototheid Antarctic fish. Sixty specimens (size 130-400g fresh weight, 22-30cm length) were caught in Terra Nova Bay, Ross Sea, and, after a period of acclimatization, were put in 200-L glass aquaria at different temperatures of 0 °C, 1 °C and 2 °C. After 1, 5 and 10 days fishes were killed and the following organs were collected and frozen at -20 °C: muscle, intestine, gills, liver and heart. The treatment of samples provided for homogenization and lyophilisation until constant weight. Lipids were extracted by petroleum ether:acetone (2:1, v/v) using microwave extraction [2]. Methyl esters of fatty acids (FAMES) were obtained from total lipids extract adding 1% of sodium methylate/methanol [3]. GC/MS analyses were performed using a temperature-programmed mode on an Agilent-6890 gas chromatograph equipped with an Agilent-5973N quadrupole mass selective detector, column CC-wax-MS (30 m, 0.25 mm, 0.25 µm). Preliminary data on FA composition of muscle showed an FA profile similar to that found in other organisms of the same specie [4]. The main FAs found were 14:00, 16:0, 16:1n7, 18:1n9, 18:1n7, 20:1n9, 20:5n3 and 22:6n3. On the average, saturated, monounsaturated and polyunsaturated FAs contributed ~20%, ~50% and ~30% of total FAs, respectively. Significant changes in FAs composition were observed in particular for an exposition of 10 days at 2 °C, with an increase of 16:0, 18:1n9, 18:3n6, and a significant reduction of 22:1n9.

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**DEEP CHEMICAL CHARACTERIZATION OF URBAN PARTICULATE MATTER**

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This communication shows a complete chemical characterization of the particulate matter in the range 10 nm to 10 µm. This task is important for understanding the effects of new technological processes on the evaluation of the air quality; simultaneously, it is not trivial considering the relative analytical implications

We will show how the main fraction of the aerosol average size distributions during different events in Rome both in winter and summer periods, is characterized by significant levels of PM<sub>2.5</sub>, especially in summertime, when the atmospheric stability conditions are numerically more than those in other period causing a pollutant accumulation: almost 75% of total PM<sub>10</sub> fraction is PM<sub>2.5</sub>.

A particular attention has been devoted to investigate the contribution of Ultrafine Particles (UFPs) on aerosol number concentration and their dynamic of formation: the trends of UFPs vs. NO<sub>x</sub> and of UFPs vs. total PAH show the primary origin of this pollutant and the narrow relationship between combustion processes and their presence in urban atmosphere. Particle formation in the nucleation mode was favored in periods with high radical oxidative activity

About the chemical characterization we determined almost 30 elements in PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub>; after, we analyzed 4 different aerosol size distribution below 100 nm for investigating the element distribution in particles extremely dangerous for the human health.

An important issue of this communication regards the comparison of these data with previous measurements performed by the authors. In particular, the concentration level comparisons of OC/EC and PM<sub>2.5</sub> (over the last two decades) and, mainly, of PM<sub>10</sub> (over the 4 last decades) will be shown.

All the samples were collected in downtown Rome; the UFPs were investigated by SMPS and FMPS analyzers (TSI, Shoreview, MN, USA) whereas the elements were determined by mean of Instrumental Nuclear Activation Analysis (INAA).

## DEGRADATION STUDIES OF HERBICIDES USED IN RICE CULTIVATION

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Rice, like other important cereals, requires a great amount of chemicals, represented especially by fertilizers and pesticides. Nowadays, pesticides formulations are designed to offer a higher selectivity and a lower persistence in the environment than the formulations used in the past. But, unlikely, a lower persistence in the environment does not necessarily correspond to a lower toxicity. In fact, it has been demonstrated that many chemicals often undergo natural degradation reactions in the environment that may lead to the formation of new species potentially more toxic and stable than the precursors [1-3].

In the present study, Imazamox, Oxadiazon and Profoxydim that are the most important herbicides used in rice cultivation of Italy were undergone to degradation studies simulating natural environmental conditions. Aqueous solutions of the species both in mix and alone were exposed to sun light irradiation in a solarbox. Also hydrolysis processes were studied preserving the solutions at dark. At prefixed times, the solutions were analyzed by using a micro liquid chromatography system interfaced to a quadrupole-time of flight (QTOF) high resolution mass spectrometer. LC-MS analysis of the samples undergone to sunlight irradiation showed a decreased intensity of the herbicide signals, more evident than in the case of the hydrolysis processes. The kinetics of the degradation were evaluated and the degradation products were also investigated by LC-MS/MS analysis.

This research has been supported by Fondazione Cariplo, grant n. 2014-1260.

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## QUANTIFICATION AND SPECIATION OF COPPER IN PLANT TISSUES BY SIZE-EXCLUSION CHROMATOGRAPHY COUPLED WITH ICP-MS DETECTION

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Copper is an essential plant micronutrient involved in numerous biochemical functions. However, above optimal concentrations copper can act as a toxin, causing nutrient loss and oxidative stress [1]. The determination of the total concentration of heavy metal is the routine method to monitor the exposure of plants to metal pollution, but there is increasing evidence that the identification, characterization and determination of the metal species, i.e. the speciation, represents a more suitable approach to investigate metals ecotoxicity [2]. The AFTER-Cu LIFE+ project aims at demonstrating the negative impact on plants of the use of copper compounds in conventional and organic agriculture. In order to study the effect of the use of copper compounds, we performed the quantitation and speciation of copper in *Nicotiana tabacum* plants (in vitro cultivation, and in *Actinidia deliciosa* and *Olea europaea* leaves (cultivation in field), treated with copper solutions at various concentrations. For this study a) we determined the total content of copper and other elements after microwave digestion of the samples followed by flow injection – inductively coupled plasma mass spectrometry (FI-ICP-MS) analysis; b) we developed a hyphenated method for the quantitation and speciation of copper in plant samples by coupling of size-exclusion chromatography (SEC) with ICP-MS. In the latter approach it is possible to investigate the complexes of copper with compounds biosynthesized by the plants exposed to metal stress (e.g. phytochelatins, metal binding proteins...etc.).

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## **RAPID CLEAN-UP STRATEGY BASED ON MOLECULARLY IMPRINTED POLYMERS FOR THE DETERMINATION OF 3-INDOLEACETIC ACID IN PLANT EXTRACTS**

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Indole-3-acetic acid (3-IAA) is a natural auxin that plays a major role in plants growth and its determination is required for understanding plants metabolic pathways. The quantitation of 3-IAA in plant extracts is very challenging due to extreme complexity of the matrix and to the low concentration levels of this analyte. [1]

In this talk a novel clean-up strategy for purification and preconcentration of 3-IAA from plant extracts is presented. The proposed method makes use of molecularly imprinted polymers (MIPs) for the sample preparation stage. A 4-vinylpyridine-based imprinted polymer was prepared using 3-IAA as template and trimethylolpropane trimethacrylate as cross-linker.

MIPs were able to bind selectively the 3-IAA whereas other molecules with a similar structure, such as tryptophan or indoleacetamide, were not retained by the polymers.

Plant tissues were extracted with 80% methanol, and then the MIPs beads were suspended in such extract. The liquid phase was discarded and 3-IAA was recovered from the MIPs with methanol washings and analyzed by HPLC with fluorescence detection. The applicability of the method was demonstrated in terms of linearity, repeatability, recovery, limit of detection and quantitation and evaluation of matrix effect.

The MIP-based approach was compared with the traditional solid-phase extraction. The two approaches were comparable in terms of recovery, but MIPs provided for a superior sample clean-up.

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**ULTRA HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY ANALYSIS OF DIFFERENT CLASSES OF ENDOCRINE DISRUPTORS IN SEDIMENTS**

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Endocrine disruptors (EDs) are a structurally diverse group of compounds that may adversely affect human health, wildlife and fisheries by interaction with the endocrine system. Some ED compounds, with different structures and properties, are found in a high variety of products commonly used in the daily life (personal care products, pharmaceuticals and in different industrial formulations). Consequently, they can be easily found in sediments, that are at strait contact with the aquatic environment [1]. Many authors have focused the attention on EDC compounds, especially on compounds differing in their nature and origin like: estrogens, perfluorinated compounds, the class of UV filters, organophosphorous flame retardants and alkylphenols. However, the selective and sensitive determination of all of these pollutants is not easy. The complex matrices and the presence of potentially interfering compounds requires efficient extraction and clean-up procedures especially for matrices, such as sediments and sludge matrices, having high content of interfering substances. Therefore the aim of this work is to develop a sensitive and simple method for the simultaneous determination of 34 different EDCs in sediment (14 estrogens, natural and synthetic, in free and conjugated form, 12 perfluorinated compounds (PFCs), 2 alkylphenolic compounds, 1 antimicrobials, 2 organophosphorous flame retardants, 2 UV filters and bisphenol A (BPA)), performance liquid chromatography coupled to tandem mass spectrometry with electrospray ionization source (ESI) working in both positive and negative mode. Due to the matrix complexity and the high amount of contaminants, a solid phase extraction method using graphitized carbon black will be optimized for an effective clean-up step. The method was validated in terms of linearity, recovery, matrix effect, precision, limit of detection and limit of quantification for all considered EDCs, and applied to the analysis of sediments from different lakes and rivers of Lazio Region.

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**IRON DISTRIBUTION IN LICHENS WITH DIFFERENT LEVELS OF MELANIZATION: A STUDY BY MEANS OF MICRO-XRF AND ICP-AES**

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The external surfaces of parmelioid lichens, and particularly the underside in contact with the substratum, are frequently dark pigmented for the deposition of melanin-like molecules formed by the polymerization of phenolic units.

Basing on their chemical composition, it was assumed that these pigments can carry out antimicrobial, antioxidant and photo-protective functions (Butler & Day, 1998). It is also known that melanins can bind some elements, such as Cu and Fe (Senesi et al., 1987). The aims of this study are: i) to evaluate the differences among the micronutrients content of 10 lichen species, characterized by a different degree of melanisation in their *cortices*; ii) to compare a non-destructive analytical technique (micro-X Ray Fluorescence spectroscopy) with a destructive one (ICP-AES).

Our first hypothesis was tested analyzing the contents of Ca, Fe, K, Mn, S and Zn in 3 groups (A-C) of 3 lobes of each species. The concentrations of the elements were determined using a micro-Xray spectrometer in order to obtain semi-quantitative data. For each species, the measurements were conducted on the upper *cortex* (A), on the lower *cortex* (B) and only for 6 species on the *medulla*, after removing the lower *cortex* (C). The content of the elements was later measured by means of ICP-AES, after digestion in HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and HF.

Furthermore, in order to evaluate the melanin content in the samples and to compare the results with that of micro-XRF and ICP-AES, a spectroscopic infrared analysis (FTIR-ATR) will be performed on a portion of the same lobes.

The partial outcomes of both micro-XRF and ICP-AES show a greater content of Fe in group B rather than in groups A and C. Such difference was less evident for Mn and Zn. This could be due to (i) the influence of other factors such as some species-specific lichen substances, (ii) an active translocation through the mycobiont hyphae towards the most active portions of the thallus, e.g. the lobe tips, and (iii) the low content of Mn and Zn in the particulate matter eventually entrapped in the lower *cortex*.

**BIOACCUMULATION OF TRACE METALS IN PLANTS GROWING NEARBY A DECOMMISSIONED Zn-Pb MINE (SALAFOSSA, NORTHEASTERN ITALIAN ALPS)**

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The Salafossa mineral body (Eastern Dolomites) was one of the largest lead/zinc-containing mineral deposits in Europe. Both metals were mainly present as sulphides (sphalerite, ZnS and galena, PbS). Mining activity started around 1550 and definitively closed in 1985.

The concentration of several heavy metals (Tl, Fe, Mn, Pb, Zn) was determined in soils and plants (*Biscutella laevigata*) from twelve sites selected outside the mine. *B. laevigata* is a "metal tolerant" species, and it often grows near mining areas, where soil metal contents are significantly higher than natural geochemical background levels.

Heavy metal total concentration in inorganic and organic (roots and leaves of *B. laevigata*) samples were determined by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) and by GFAAS (Graphite Furnace Atomic Absorption Spectroscopy) after total mineralization. In addition, metal bioavailability in the soil - including the *B. laevigata* root system (rhizo-soil) - was estimated by using a DTPA (Diethylene Triamine Penta-acetic Acid) extracting solution. Then, to assess absorption and translocation processes of heavy metals, resulting in their bioaccumulation, two indices were calculated: the Enrichment Factor in roots (E<sub>Fr</sub>) and the Translocation Factor (TF). For both indices, a >1 value denotes an enrichment of the metal in the roots or its translocation to the upper tissues.

Results showed that metals were present in a chemical form available for absorption by the plants roots. High concentrations of the metals were found in the roots and leaves of *B. laevigata*, and these concentrations were higher than those in the corresponding rhizo-soil. The calculated indices showed that E<sub>Fr</sub> and TF were >1 only for Tl, reaching a maximum value of 60 for E<sub>Fr</sub> and 11.6 for TF. Conversely, the other metals did not show significant bioaccumulation (E<sub>Fr</sub><1) and they showed TF>1 only at a few sites.

This study showed the ability of *B. laevigata* to absorb metals from the soil and to accumulate them in the roots and/or translocate them to the aboveground biomass, especially Tl, thus representing a good indicator of Tl bioavailability in the rhizo-soil of the study area.



**ORGANIC BIOMARKERS CHARACTERISATION IN PEAT SAMPLES**

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N-alkanes, n-alkanoic acids are synthesized as part of the epicuticular leaf wax of plants. They can be used as paleoenvironmental proxies thanks to stability and weak solubility in water, especially for the long chain n-alkanes that are present only in leaves. The study of modern plants shows a clear predominance of chains with odd carbon number in n-alkanes and of even chains in n-alkanoic acids: this information could be used as indicator of the origin of molecules (natural vs petrogenic) and of bacterial degradation. Characteristic n-alkanes fall in the range C<sub>15</sub>-C<sub>31</sub>: the distribution pattern and dominant chain lengths of n-alkanes and n-alkanoic acids can be used in a multi-proxy analysis in order to reconstruct the composition of plant population and climate fluctuations [1].

Although the instrumental analysis of n-alkanes, normally performed by GC-FID, is widely employed, the characteristics of complex matrices such as peat require particular care in the extraction and purification procedures. In this work, GC-MS (Agilent 7890 – 5975c) methods for the detection of C<sub>10</sub> to C<sub>36</sub> n-alkanes and C<sub>11</sub> to C<sub>24</sub> n-alkanoic acids have been developed. The extraction was carried out by Pressurized Liquid Extraction PLE using a DCM:n-hexane mixture. Extracts were subsequently concentrated under a gentle stream of nitrogen and the clean-up was performed on silica gel SPE cartridges, collecting an apolar and a polar fraction separately, by eluting samples with a mixture of n-hexane:DCM followed by DCM:MeOH. Literature data often report palmitic and stearic acids as dominant species in samples, but rarely blank values are discussed [2]. In the present work, large amounts (ng to tens of ng) of C<sub>16</sub> and C<sub>18</sub> have been detected in laboratory blanks and mainly in SPE tubes, therefore requiring a strong conditioning with 40 mL of each solvent. The fractions were re-concentrated to about 100 µL and, before GC-MS analyses, the polar fraction was derivatized at 60°C. The method was finally tested on a small batch of samples from a peat bog located in the Dolomites.

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**MELTING OF ANTARCTIC LAKES: SEASONAL INFLUENCE ON POPS AND AMINO ACIDS DYNAMICS**

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Antarctica is almost entirely covered by an huge ice-sheet. In limited coastal areas, during only a short summer period, small and shallow seasonal lakes are fed by melted ice and snow. These have no or limited outlets and lose summer meltwater through evaporation or sublimation, accumulating solutes and particulate material from the catchment areas. The study of the effects of ice melting linked to the seasonal evolution of Antarctic lakes constitutes an experimental challenge. The waters of four lakes in Northern Victoria Land (Edmonson Point 14 and 15A, Inexpressible Island 10B and Tarn Flat 20) were sampled at the beginning and at the late/complete melting of ice, with the aim to highlight the seasonal evolution and amplification phenomena [1,2]. Both persistent organic pollutants (POPs, i.e. PCBs and PBDEs) and primary production indicators, such as L- and D- amino acids were determined in water samples. Combining the information deriving from the two classes of tracers allowed to obtain a more detailed indication of sources and processes. Samplings were carried out during the 2011-2012 austral summer. Pre-analytical steps were performed in the laboratories in Antarctica with particular attention to avoid contamination risks. PCBs and PBDEs were later analyzed by HRGC coupled to HRMS and LRMS (MAT95XP, Thermo Finnigan; 7890A-5975C, Agilent Technologies). The quantification of amino acids was performed using an HPLC with a chiral column coupled with an API 4000 triple quadrupole (AbSciex), achieving very low detection limits (4 - 200 ng L<sup>-1</sup>). PCBs showed a general slight increase during the melting season, while the behaviour of PBDEs resulted more complex, reflecting the influence of similar sources. The study of amino acids highlighted the role of local fauna, in particular in lake Edmonson Point 14, since the inputs of nutrients from seabirds greatly promoted the primary growth. Also the presence of bacteria was confirmed by relevant concentrations of D-alanine. An increase was observed also in lake 10B, probably due to marine inputs or evaporation linked to strong katabatic winds, while dilution phenomena were prevalent during the melting in the other lakes. Funds were provided by PNRA 2013/AZ2.05.

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**OCCURRENCE OF FRAGRANCES IN THE CANALS OF VENICE**

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Perfumes are ubiquitous in daily life. The majority of cosmetics, toiletries and a variety of household and Personal Care Products (PCPs) contain fragrance materials. In spite of their widespread use, little is known on the environmental fate of these compounds. The aim of this study is to partially fill this gap of knowledge. Commercial fragrances (provided by Givaudan<sup>®</sup>) were selected owing to their stability and persistence properties. The knowledge about the environmental distribution and fate of these compounds is very limited [1] or absolutely lacking. The Venice lagoon is a perfect macrocosm laboratory to study PCPs: the city of Venice sits in the middle of it, but, as the historical center is almost completely lacking a sewerage system, PCPs are discharged directly into the canals. Water samples from different canals were collected and analyzed.

A new analytical method was developed and validated: extraction of unfiltered water samples was performed using Oasis<sup>®</sup> HLB Cartridges (Waters). After solvent elution and concentration under gentle nitrogen stream, samples were analyzed by HRGC-LRMS (Agilent 5890-5975C). Quantification was performed using phenanthrene <sup>13</sup>C as internal standard and the results were corrected using instrumental response factors.

Salicylates resulted the most abundant and widespread class of compounds. More precisely, Amyl Salicylate, Hexyl Salicylate and Benzyl Salicylate were found in all the samples, ranging from 15 to 251 ng L<sup>-1</sup>. Benzyl Salicylate, also used as UV-filter [1], is included in the EU list of allergenic fragrances and was recently found to have an estrogenic activity comparable to Bisphenol A (BPA) [2]. Less abundant, but still present, were Oranger Crystals, Ambrofix and Peonile (commercial names). To the best of our knowledge, this is the first detection of these compounds in environmental samples from the Venetian Lagoon.

This cutting-edge study on the selected fragrances as new emerging pollutants constitutes the starting point to recognize their occurrence and fate in the environment.

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## **COD AND TPH ANALYSIS IN SLOPS TREATMENT'S EXPERIMENTAL PLANTS: ANALYTICAL PROBLEMS.**

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In the last years, the persistence and accumulation of xenobiotic compounds in the environment created many disposal problems of oily wastewater generated by ships, mainly in engine-rooms (bilge waters) and by cleaning of tanker (slops). The high salinity levels (up to 25.000 mgL<sup>-1</sup>) and the pollutants concentration, both limit the chances of discharge into the sewer systems and address the disposal of these wastewaters to the sea. For these reasons it is necessary to treat such wastewater efficiently before discharging [1]. As a part of a broader project concerning slops treatments, this work addresses issues related to the analytical methods of the COD and TPH parameters, chosen under the provisions of Italian Legislative Decree 152/06, that implements the European directives on environmental protection. In the COD analysis the greatest difficulty was the high salinity levels corresponding to high chlorides levels. Chlorides cause a positive interference in the measurement, and this interference during the analysis of COD was investigated at various concentrations of mercury in order to try to minimize the use of this reagent that causes many problems of safety and disposal, and at different times reaction [2][3][4]. The major problems in TPH analysis concerned correct setup of the gas chromatographic separation, high variability in sample composition and the high capacity of the sample to form emulsions during the liquid-liquid extraction procedure.

This paper reports the results of the analysis of COD and TPH and the problems related to the development of a suitable analytical method for the analysis of these specimens.

This study is part of STITAM European project, created with the aim to develop innovative technologies for the treatment of liquid wastes of navigation, in order to better safeguard marine environment.

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## **HEAVY METALS AND PLATINUM GROUP METALS DETERMINATION IN OYSTERS, MUSSELS AND CLAMS AS BIOMONITORS OF POLLUTION IN THE ADRIATIC AQUATIC SYSTEM.**

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Heavy metals are very dangerous pollutants owing to their bioaccumulation and toxicity, and in particular platinum group metals are new emerging anthropic traffic-related pollutants. To establish reasonable water quality criteria it is therefore necessary to determine these metals at trace and ultra-trace level, especially in aquatic ecosystems. Moreover, toxic metals accumulate in certain marine species and thus enter the aquatic food chain. In particular oysters, mussels and clams sequester and concentrate several metals from their aqueous environment, possibly becoming dangerous to human health in consequence of their consumption. These filtering organisms require particular attention and inspections before being sold on the market: an adult organism is able to filter even up to  $5 \text{ L h}^{-1}$ , depending on its weight.

In addition to this important and fundamental aspect of public health, the determination of toxic metals in mussels and clams, that are not only filtering organisms but also sessile species, can be usefully employed for bio-monitoring campaigns, that evaluate the long-term trend of the pollution load of an aquatic ecosystem: this information evidently cannot be provided by punctual determinations.

For completely mapping environmental pollution, the sampling duration and cadence are very important. In our opinion, the use of bio-monitors, just proposed by several authors, but certainly not scientifically supported, is possible only in the case of a long sampling plan. In any case, the metal determination in mussels and clams must be evidently accurate and especially characterized by very low limits of detection.

The present work reports and discusses the different analytical methodologies for the voltammetric and spectroscopic determination of heavy metals and platinum group metals in oysters, mussels and clams sampled near the northern Adriatic coast.

## ANALYTICAL AND PREPARATIVE PYROLYSIS TO INVESTIGATE THE CONVERSION OF PROTEINACEOUS BIOMASS INTO HYDROCARBONS BY ZEOLITE CRACKING

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Biomass is the only renewable resource towards carbon-based fuels. Pyrolysis is a viable route to produce a liquid fuel (bio-oil) from solid biomass, and bio-oil from fast pyrolysis of woody biomass is expected to enter the market [1]. In the case of protein-rich substrates, such as algae, the abundance of nitrogen is a major drawback (e.g. chemical NO<sub>x</sub>). Catalytic pyrolysis, specifically zeolite cracking with H-ZSM-5, has been investigated to transform proteinaceous biomass into a liquid fuel with low N content [2]. Analytical pyrolysis (Py-GC-MS) is the technique of choice to gather preliminary information on the process (e.g. feedstock effect, catalyst performance) [3]. Few studies have compared Py-GC-MS with preparative pyrolysis and evaluated the predictive potential of Py-GC-MS [4]. In this study, four biomasses with different protein content (pine wood, microalgae spirulina *A. platensis*, macroalgae *U.lactuca* and marine fishing residue) were investigated by Py-GC-MS and preparative pyrolysis.

Py-GC-MS was performed with a CDS pyroprobe platinum heated filament on dried biomass mixed with H-ZSM-5. Preliminary experiments with the microalgae *D.communis* showed that cracking into aromatic hydrocarbons became significant at 1:10 biomass:zeolite ratio and at pyrolysis temperatures higher than 400 °C. Py-GC-MS were conducted at 600 °C and 1:10 biomass:ZSM-5(Si/Al 45) ratio. The pyrograms were dominated by alkylbenzenes, principally toluene, followed by alkylated naphthalenes. Nitrogen-containing compounds NCC (aromatic and aliphatic nitriles, indoles, pyrroles, carbazoles) featured the pyrograms from algae and fishing residue. Zeolite cracking was conducted with a bench reactor under conditions similar to Py-GC-MS. Bio-oil, aqueous fraction, char and coke were analysed. Bio-oil was obtained in low yields, but with a composition dominated by alkylated benzenes typical of gasoline and a significant reduction of N. The lower proportion of NCC in bio-oil with respect to Py-GC-MS was attributed to the preferential distribution of functionalized compounds into the aqueous fraction.

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## ADSORPTION OF RARE EARTH IONS ONTO ZEOLITES

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The global consumption of rare earth elements (REEs) has grown rapidly in the last decade due to their use in many different technological processes, including the production of computers, plasma and LCD screens, cell phones, cameras, etc. Different methodologies have been proposed for the recovery of REEs from wastes of different origin, which are mainly based on liquid/liquid extraction and precipitation. These techniques, however, very often require harsh conditions and the consumption of very large volumes of solvents. In comparison, liquid-solid extraction has been considered a simpler and greener alternative [1].

In this work the adsorption of two REE ions, Neodimium (Nd) and Itrium (Y), on different zeolites (L, 13X and chabazite) has been investigated by means of batch equilibrium experiments (both single component and competitive). Due to their structural characteristics [2,3], zeolites have been employed in several applications that suggest that their use for the selective adsorption of rare earth ions could be very promising. One example is the use of zeolites for the removal of heavy metals from aqueous solutions. The adsorption capacity and kinetics of zeolite-L, zeolite-13X and chabazite towards Nd and Y ions have been evaluated by employing solutions of both ions with concentrations ranging from 5 to 300 mg/L and different (a) zeolite/solution ratio, (b) pH and (c) temperature.

The results have shown that, among the considered zeolites, zeolite 13X has the largest saturation capacity, with a maximum at pH 5.5 for both elements. Together with the information that the adsorption kinetics is fast enough, it can be concluded that adsorption on zeolites deserves to be explored as a new, potentially very competitive alternative for REE purification process.

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**PHOTOCATALYTIC HYDROGEN GAS PRODUCTION FROM AQUEOUS CELLULOSIC BIOMASSES COUPLED WITH SOLID STORAGE BY INTERMETALLIC HYDRIDES AND METAL ORGANIC FRAMEWORKS: A PILOT STUDY**

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The possibility of direct solar production of hydrogen gas ( $H_2$ ) from polysaccharide suspensions at ambient conditions is of great practical importance in the framework of a sustainable economy. As the most abundant biopolymer on the Earth, cellulose (CLS) is attracting the interest of the scientific community with regard to its conversion into biofuels [1] and  $H_2$  [2]. Basing on our previous lab-scale results about the photocatalytic  $H_2$  evolution from water-suspended cellulose [2], in this work we investigated the feasibility of  $H_2$  evolution using a pilot photoreactor (0.5 L). Photocatalytic experiments were performed by UV-Vis irradiation (medium pressure Hg lamp, 125 W) of aqueous CLS samples (2.1 g biomass, 310 mL tap water, native pH) in the presence of  $2 \text{ g L}^{-1}$  Pt/TiO<sub>2</sub> (Pt 0.3 wt%) as the catalyst, obtaining  $H_2$  yields up to ca. 0.36 mmol. Interestingly, considerable amounts of  $H_2$  were obtained in the subsequent irradiation cycles; in fact,  $4 \times 6$  h irradiation provided up to ca. 1 mmol  $H_2$ , at ambient temperature and pressure. Our final aim is setting up a simple and working system that couples production of  $H_2$  from costless and renewable sources (process water and biomass) with its subsequent solid state storage employing novel, efficient materials able to work under mild temperature and pressure conditions. At this purpose, experiments are ongoing on waste cellulosic biomass (i.e. raw rice husk) as the sacrificial agent, and low temperature catalyzed intermetallic hydrides or novel metal organic frameworks as hydrogen tank.

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## MONITORING THE STRESS RESPONSE OF ESCHERICHIA COLI TO NANOANTIMICROBIALS BY MALDI-TOF MASS SPECTROMETRY

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Metal Nanoantimicrobials (NAMs) are frequently used as bioactive systems with low human and environmental toxicity for applications in food and textile industries, biomedicine, and other fields [1]. Most NAMs provide controlled release of metal ions, eventually slowing down or completely inhibiting the growth of undesired microorganisms [2]. NAM bioactivity usually implies the damage of the cell membrane, its structural and functional changes, and the nanoparticle (NP) consequent penetration into the cell. To date, a complete correlation between the material properties (bulk and surface chemical composition, structure and morphology) and the degree of antimicrobial efficacy is still missing. A careful study, at the molecular level, to monitor the real time changes of microorganisms as a response to various NAM expositions, would respond to these aims.

The present work describes the application of MALDI-TOF mass spectrometry as a powerful tool [3,4] to obtain protein and lipid profiles of cell membranes from bacterial strains treated with copper antimicrobial agents, such as soluble salts (chosen as reference) and different NAMs. At first, the main critical experimental parameters (i.e. cell concentration, selection of the MALDI matrix, optimal solvent composition, sample preparation method) for the MS analyses were optimized on an *Escherichia coli* ATCC 25922 strain. The resulting procedure was then used to achieve protein/lipid fingerprints from intact *E. coli* after exposition to different Cu nanoparticle loadings. The final aim of the work is to develop, through the understanding of the microorganism response mechanisms, new NAMs with tunable activity in terms of low cytotoxicity and high antimicrobial efficacy.

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**PROTON-TRANSFER OR ELECTRON-TRANSFER MATRIX FOR MALDI TOF MS ANALYSIS OF CYCLIC TETRAPYRROLE DERIVATIVES**

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Cyclic tetrapyrrole derivatives, as porphyrins, chlorins, corrins, and phthalocyanines, are a large family of molecules containing four pyrrole rings usually coordinating a metal ion (i.e., Mg, Cu, Fe, Zn, etc.). These structures are present in numerous natural compounds as green pigments in chloroplasts [1] or red pigments (heme b and c) in hemoglobin, myoglobin and cytochrome c [2]. Porphyrins, phthalocyanines, and corroles complexes are also efficient catalysts for many reactions [3].

Cyclic tetrapyrroles and related compounds are usually investigated by high performance liquid chromatography coupled with mass spectrometry (LC-MS) even if, due to the necessary sample treatment, routine analyses of large numbers of samples become unaffordable [4]. In this context, matrix-assisted laser desorption/ionization (MALDI) time-of-flight (ToF) MS can offer a fast and selective identification of these compounds thanks to well-recognized features, such as rapid and easy sample preparation, tolerance to salts, and high sensitivity. So far, the analysis of cyclic tetrapyrrole derivatives by MALDI-ToF MS has not been fully established. Considering the extensive conjugation of these systems and the nature of the coordinating metal cation, different ionization pathways can occur during the MALDI process. Thus, the properties of the MALDI matrix (proton-transfer or electron-transfer) can be crucial to successfully achieve structural information on these compounds [5]. Here, we report the characterization of some representative cyclic tetrapyrrole-derivatives by MALDI-ToF/ToF MS analyses, including chlorophylls (*a* and *b*), vitamins B12, heme, phthalocyanines, etc. upon proper matrix selection.

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**CHEMILUMINESCENT LATERAL FLOW IMMUNOASSAY FOR QUANTITATIVE DETECTION OF HUMAN SERUM ALBUMIN IN URINE EMPLOYING A CARTRIDGE WITH INTEGRATED AMORPHOUS SILICON PHOTODIODES**

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Lateral Flow ImmunoAssay (LFIA) technology is one of the most successful for Point-Of-Care (POC) applications, which are aimed at enabling analysis execution directly where the sample is obtained. We have recently shown that coupling LFIA with chemiluminescence detection (CL-LFIA technology) greatly improves analytical performance in terms of detectability and ability to obtain quantitative information.

Herein we describe the development of a simple, accurate, rapid and ultrasensitive biosensor based on a CL-LFIA method for quantitative detection of human serum albumin (HSA) in urine samples. The method employs a ready-to-use polydimethylsiloxane (PDMS) microfluidic cartridge that contains all the reagents necessary for the analysis and an array of hydrogenated amorphous silicon (a-Si:H) photodiodes as CL detector.

The analytical method is based on a competitive immunoassay using peroxidase-HSA conjugate which is detected by adding the CL luminol/enhancer/peroxide cocktail.

The immunoassay conditions were optimized to generate an assay with a detection limit and dynamic range suitable for measuring physiological levels of HSA in urine samples and their variation in different diseases, to provide a valuable tool for the diagnosis and typization of diabetes.

**DETECTION OF VIRAL DNA BY ISOTHERMAL AMPLIFICATION AND CHEMILUMINESCENCE GENE PROBE HYBRIDIZATION ASSAY IN A SELF-STANDING MICROFLUIDIC CARTRIDGE**

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The development of portable self-standing analytical devices for point-of-care (POC) real-time analysis of samples and timely accurate diagnosis is one of the most recent and active research field in analytical chemistry. With this respect, chemiluminescence (CL)-based biosensors are particularly attractive, since they combine high detectability with the requirement of simple and compact instrumentation.

As concerns infectious disease diagnosis, the gold standard analytical techniques are most often based on nucleic acid amplification followed by sequence-specific detection of amplicons. In order to facilitate the scaling down of nucleic acid amplification techniques in lab-on-chip devices, several isothermal DNA amplification techniques have been proposed.

In this work, we describe the development of a POC device portable microfluidic cartridge with integrated hydrogenated amorphous silicon (a-Si:H) photosensors and its use for multiplex detection of parvovirus B19 genotypes, exploiting oligonucleotide array capture and chemiluminescence (CL) detection. The cartridge is composed of a glass slide on which an array of thin film a-Si:H photosensors has been deposited on one side, while the opposite side has been chemically derivatized to enable B19 DNA hybridization and detection. The cartridge is completed with a polydimethylsiloxane (PDMS) microfluidic layer. Different types of isothermal DNA amplification systems have been evaluated, namely loop mediated isothermal amplification (LAMP) and nucleic acid sequence-based amplification (NASBA). Results, as compared with those obtained by reference laboratory instrumentation, demonstrate the possibility to reach high detectability and specificity in a POC format.

## HOLLOW-FIBER FLOW FIELD-FLOW FRACTIONATION WITH MULTI-ANGLE LASER SCATTERING FOR AGGREGATIONS STUDIES IN COMPLEX PROTEINS

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The protein aggregation phenomena represent a crucial issue in different biotechnological applications [1]. Protein aggregation is a common biological phenomena occurring during physiological and pathological conditions. A method capable of separating protein aggregates based on their biophysical properties would allow further analysis on how protein sequence/structure determine their tendency to aggregate, how different post-translational modifications affect unfolding and aggregation and the proteomic machinery associated with their degradation. Moreover, the bioactivity and the stability of protein-based pharmaceuticals are closely related to the maintenance of their complex structure, however, influenced from many external factors that can cause degradation and/or aggregation. The presence of aggregates in these drugs could reduce its bioactivity and bioavailability and induce immunogenicity. The rapid development of protein-based pharmaceuticals highlights the need for robust analytical methods to ensure their quality and stability.

Among the techniques for the size-characterization of proteins, field-flow fractionation (FFF) represents a competitive choice since its soft mechanism due to the absence of a stationary phase and the higher dimensional range of applications from nanometer to micrometersized analytes. The microcolumn variant of FFF, the hollow-fiber flow FFF (HF5), was on-line coupled with multi-angle light scattering and methods for the characterization of aggregates with high reproducibility and low limit of detection in complex samples such as cell lysate or therapeutic proteins was demonstrated [2].

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[2] Zattoni A, Casolari S, Rambaldi DC, Reschiglian P. *Curr Anal Chem* 3(4) (2007) 310-323

## **ASSESSING THE POTENTIAL RISKS OF SILVER NANOPARTICLES IN ANTIMICROBIAL APPLICATIONS, USING MINIATURIZED FLOW FIELD-FLOW FRACTIONATION AND MULTI-ANGLE LIGHT SCATTERING**

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Colloidal silver nanoparticles are known for their antimicrobial applications in everyday life items, and their use in commercial products is increasing; to investigate how and if nanoparticles may present harm for the environment and organisms, a characterization of their behavior in environmental and physiological media is required besides size, shape, activity and stability assessment. Hyphenation of multiangle light scattering (MALS) detection with size-based separation methods presents a multidimensional platform that can enhance accuracy for analysis of complex NP samples, and hollow-fiber flow field-flow fractionation (HF5) is particularly suited for this task. In HF5, separation occurs between species with different hydrodynamic radius. MALS detection, on the other hand, allows for the calculation of particle root mean square radius, which depends on particle compactness. Particle shape is determined correlating these values.

We developed HF5-UV-MALS methods able to fractionate silver NPs in aqueous media, determine their size and shape distribution, study aggregation phenomena, separate unbound constituents from the functional NPs, and correlate NP size with their spectroscopic properties. We have tested new methods for analysis of metal release through fiber filtration to improve full characterization of metal-based nanoparticles, in order to study both their functional effectiveness and potential hazards.

## **TOWARDS “TRUE” ARTIFICIAL ANTIBODIES BY MOLECULAR IMPRINTING**

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Despite the undoubted success of natural antibodies in widespread analytical applications developed in the last fifty years, there are several shortcomings that yet limit their practical applications. High costs of production, low batch-to-batch reproducibility and instability in non-aqueous environments push toward the development of alternative binding systems based on man-made receptors.

Developing ‘wholly synthetic’ macromolecular structures that can mimic natural antibodies presents a considerable challenge for chemists, who lack the biological machinery used in nature to assemble such biomacromolecules with high precision. In addressing this challenge, molecularly imprinted polymers (MIP) represent the most successful achievement, and in the last twenty years they have been frequently described by many authors as “artificial antibodies” or less commonly “plastibodies”.

However, despite the rapid development of MIP-based technologies as a research hotspot and the undeniable success of these polymers in several analytical applications such as solid phase extraction, there are serious limitations to the use of MIPs as an efficient alternative to antibody-based technology in application fields such as sensoristics and immunoassay.

Here we report the current status of MIP technology, with particular emphasis on present challenges involving dimensional downscaling, difficult biomacromolecule imprinting and incompatibility with aqueous media, and the possible strategies to be implemented in order to overcome these technological bottlenecks with particular emphasis on the solid-phase synthesis of imprinted nanogels and the use of proteins as aqueous-compatible nanoscaffolds for molecular imprinting.

## A HIERARCHICAL APPROACH AS NEW STRATEGY FOR MOLECULAR IMPRINTING OF BIOMACROMOLECULES

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The most popular method for obtaining molecularly imprinted polymers consists in a bulk polymerisation which produces a monolithic material that has to be crushed and sieved to obtain particles of the desired size distribution. Despite being a convenient approach when template is represented by low-mass molecules, it completely fails when template is represented by a biomacromolecule such as a polypeptide or a protein. The impossibility to work in organic solvents due to the strongly polar nature of biomacromolecules and the difficulty to extract efficiently the large template after the polymerization process requires alternative approaches. To overcome these drawbacks several methods based on the direct synthesis of macroporous imprinted beads or on the surface-confined polymerization on solid supports have been proposed in recent years. Unfortunately, such approaches cannot cope well with the impossibility to imprint proteins starting from homogeneous pre-polymerization mixtures.

Starting from a methodology previously developed in our laboratory to efficiently imprint low-mass templates [1], we report here an analogous tailor-made approach for very large and strongly hydrophilic templates. This approach consists in the following steps: (i) preparation of macroporous silica monoliths by controlled hydrolysis of silane precursors in microplate wells; (ii) covalent grafting of template protein onto the surface of the macropores; (iii) synthesis of a silica-polymer composite by filling grafted macropores with an imprinting mixture and subsequent radical thermopolymerization; (iv) dissolution of the silica support by corrosion with ammonium fluoride.

Here we describe the preparation of ovalbumin (OVA, mw. 45 KD) imprinted monoliths and the characterization of their binding properties in terms of binding capacity and selectivity towards proteins. The experimental results show that the use of sacrificial silica monoliths as vessels for the synthesis of molecularly imprinted monoliths is a very efficient alternative to emulsion or surface polymerization, and it is particularly convenient when a fragmental template approach is needed (peptides) or when compatibility between template molecule and porogenic solvent does not exist at all (proteins).

[1] C. Giovannoli, L. Anfossi, F. Biagioli, C. Passini, C. Baggiani, *Microchim. Acta*, 180 (2013) 1371-1377



**NON-INVASIVE STRESS ASSESSMENT IN DOGS BY MEASURING CORTISOL IN SALIVA**

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Recently, studies have focused on the welfare of domestic, companion, and experimental animals. Dogs are used not only as companions but also as working animals (e.g., guide dogs, police dogs, or laboratory animals for research). It has been recognized that stress deteriorates performance of dogs as well as their welfare. Periodic evaluation of stress in dogs is important to monitor their welfare, and a simple, accurate method to evaluate the stress experienced by these dogs is necessary for this evaluation. Plasma cortisol levels are recognized as the marker of the hypothalamic-pituitary-adrenal response to stress; however, blood collection is an invasive procedure that requires skilled technical capabilities and has been shown to act as a source of stress itself. Because saliva sampling is non-invasive and salivary cortisol is highly correlated with plasma cortisol, salivary cortisol can be used as a measure of adrenocortical activity at convenience. Indeed, salivary cortisol has been used to evaluate stress response in studies of welfare, reaction to stress and human–animal interactions in dogs [1].

Several analytical methods are available for human salivary cortisol determination, including chromatographic-based detection. Enzyme-linked immunosorbent (ELISA)-methods are also available and are widely employed in routine analysis, because of their simplicity and rapidity. Among rapid diagnostic methods, immunochromatographic strip test (ICST) technology is attracting a growing interest for veterinary applications, mainly because of allowing very rapid, simple, *in situ* analyses to be carried out. We developed a quantitative ICST for measuring cortisol in canine saliva and we applied it for measuring cortisol levels in 40 subjects. Agreeing results with a reference ELISA kit were obtained. The ICST is rapid (provide results within 10 minutes), sensitive (LOD 0.8 nM), accurate (recovery: 82-115%) and executable outside the laboratory by non-trained personnel, thus applicable for stress assessment of dogs i.e.: in veterinary clinics.

[1] N.A. Dreschel, D.A. Granger, *Horm Behav* 55 (2009) 163-168.

## NANOPOROUS FUNCTIONALIZED GOLD FOR BIOSENSING APPLICATIONS

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Health promotion and disease prevention are included in the most important challenges of Horizon2020. Thus, the development of diagnostic tools based on sensible and selective analytical approaches can be of tremendous importance for the Europe development of boosting cutting-edge biotechnologies as future innovation drivers and they can be of crucial importance for helping european industry to stay at the front line of innovation. Main fields of interest mainly concern the set-up of devices based on accessible and affordable detection of pathogenic agents, disease markers, food contaminants or environmental toxicants. As alternative to the enzyme-linked immunosorbent assay (ELISA) that is considered a gold standard for routine and target-driven analysis, more recently a lot of efforts have been dedicated to develop fast quantitative lateral flow immunoanalysis (LFIA) devices for rapid point-of-care testing (POCT), even though not always competitive with ELISA in terms of sensitivity and robustness. Here, we present the preliminary results related to the development of a new highly customizable bio-sensing strategy based on the use of a novel nanoporous Au functional nanomaterial (NPG). This approach aims to synergistically exploit the high selectivity of antibodies and the tremendous single-molecule sensitivity of surface enhanced Raman spectroscopy (SERS), for the versatile detection of a large body of target compounds, ranging from low mass organic molecules to large proteins. In order to preliminary assess the ability of NPG to be covalently functionalized with a anti-human serum albumin antiserum raised in rabbit (pAb anti-HSA), two different synthetic routes were considered. The first one was based on the preliminary gold functionalization with cysteamine and the subsequent immobilization of the immunoglobulins on the self-assembled monolayer via EDC/NHS method. The second was based on the gold functionalization with mercaptopropionic acid and the subsequent immobilization of the immunoglobulins via NHS/DIC method. The functionalized gold surfaces were tested by using a FITC labeled human serum albumin and a HRP-labelled anti-rabbit antiserum in order to assess the binding performances.

**BIOMOLECULAR CORONA MAKES ANIONIC NANOPARTICLES LESS ATTRACTIVE FOR IMMUNE CELLS**

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When injected in a biological milieu, a nanomaterial rapidly adsorbs biomolecules forming a biomolecular corona. The biomolecular corona changes the interfacial composition of a nanomaterial giving it a biological identity that determines the physiological response. Characterization of the biomolecular structure and composition has received increasing attention mostly due its detrimental impact on the nanomaterial's metabolism in vivo. [1] It is generally accepted that an opsonin-enriched biomolecular corona promotes immune system recognition and rapid clearance from circulation. Here we explored the structure and composition of the protein corona recruited by anionic lipid NPs made of 1,2-dioleoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (DOPG) and silica NPs upon interaction with human plasma (HP) by using dynamic light scattering and nanoHPLC-MS/MS. On the light of the bioinformatic analysis of the proteomic data, we demonstrate that both the biomolecular coronas, despite being enriched with immunoglobulins, complement factors and coagulation proteins, reduced the cellular uptake by 264.7 RAW cells with respect to pristine NPs. We hypothesize that the ability of immunoglobulins and complement proteins to bind receptors of immune cells can be impaired by other protein corona components. Our results indicate that, of the proteins adsorbed to NPs, only a minor fraction will have relevant functional motifs facing externally, away from the nanoparticle surface. Obvious implication is that nanoparticle–corona complexes could interact with target cells, immune cells and other circulating molecules more or less favorably than bare NPs depending on the exact location of corona proteins. Our results suggest that correct prediction of the NP's fate in vivo will require more than just the knowledge of the biomolecular corona composition. Validation of efficient methods for mapping protein binding sites on the biomolecular corona of NPs is an urgent task for future research [2].

[1] M. P. Monopoli, D. Walczyk, A. Campbell, G. Elia, I. Lynch, F. Baldelli Bombelli, K. A. Dawson *Journal of the American Chemical Society* 133 (2011) 2525-2534

[2] P. M. Kelly, C. Åberg, E. Polo, A. O'Connell, J. Cookman, J. Fallon, Z. Krpetić, K. A. Dawson, *Nature nanotechnology* 10 (2015) 472-479.

**PROTEOMIC STUDY OF HUMAN COLON ADENOCARCINOMA CELLS EXPOSED TO SIMULATED MICROGRAVITY**

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National Aeronautics and Space Administration (NASA) is currently planning a manned mission to Mars in the 2030s. Nevertheless, several issues still must be solved. Different scientific studies focus on health problems that astronauts might face during a long stay onboard an interplanetary space vehicle. Indeed, besides radiations and stressful environment, space missions expose the crewmembers to microgravity, that affects several cellular functions such as signal transduction [1] and protein expression [2]. Among the alterations that might occur, changes in the gastrointestinal (GI) apparatus and related gut inflammatory states are of particular relevance. Microgravity could lead to decreased GI motility and reduced dietary intake [3]. Such possible alterations must be detected to take the necessary measures to avoid negative consequences to the crewmembers' health. To investigate microgravity effect on GI motility human colon adenocarcinoma cells (Caco-2) were selected as model of the intestinal barrier. Considering the biological effects that microgravity could have on protein expression, we compared protein profiles of Caco-2 cells grown in simulated microgravity and in normal gravity conditions. Caco-2 cells were exposed for 0, 24 and 72 hours to microgravity conditions using Rotary Cell Culture System (RCCS-1-HARV, Synthecon). Cells proteome was fractionated into four sub proteomes of decreased complexity exploiting the differential solubility of certain subcellular compartments (cytosol, membranes, nucleus, cytoskeleton). Cells fractions were digested and tryptic peptides analyzed through the modern shotgun proteomics approach. A label-free quantitative nano-liquid chromatography-tandem mass spectrometry analysis was performed. Studying global responses to perturbations in terms of protein quality and quantity, allowed the investigation of expression of proteins involved in regulatory molecular mechanisms of GI motility and inflammatory states process.

[1] L.Vincent, S.Y.Rabbany, *Ann. Biomed Eng.* 33 (2005) 350-364.

[2] D.Grimm, P.Wise, M.Lebert, P.Richter, S.Baatout, *Expert Rev Proteomics* 8 (2011) 13-27

[3] J.R.Lackner, P.Dizio. *Exp Brain Res* 175 (2006) 377-399

## DIFFERENTIAL ANALYSIS OF THE PROTEIN CORONA COMPOSITION ONTO LIPOSOMES IN STATIC AND DYNAMIC CONDITIONS

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In the recent years, nanomedicine is attracting strong attention due to the great development of nanotechnologies for diagnostic and therapeutic treatment of diseases. In particular, in the last two decades non viral vectors, such as liposomes, have attracted a growing interest either for driving pharmaceuticals molecules or as gene vectors for the treatment of tumors. When nanoparticles enter into blood circulation, plasma proteins are adsorbed onto their surface to form a “protein corona” [1]. These interactions with blood biomolecules have been shown to have an essential role in nanoparticle biodistribution. The knowledge of the corona composition provides a means by which nanoparticles can be targeted to specific cells (active targeting). However, until now, all the studies upon this interaction have been performed in static conditions; for a deeper knowledge is necessary to investigate the incubation in dynamic conditions which closer mimic the reality, being the protein corona composition is a dynamic phenomenon, affectable by presence of stream. In order to mimic dynamic conditions, a tunable peristaltic pump with silicon tubes ( $d_i$  1.6 mm, total length 250mm) has been employed with an optimized flow rate chosen to mimic the human abdominal aortic flow velocity ( $\sim 40 \text{ cm s}^{-1}$ ). The aim of the present work was the comparison and characterization of protein corona adsorbed onto multicomponent (MC) liposomes in static and dynamic conditions because the knowledge of such proteins could be useful to elucidate the differences between the two model systems. For this purpose, we have employed a label-free quantitative shotgun proteomics approach based on “in-solution” proteolytic digestion of the whole protein mixture and determination of the resulting peptides by nano-high-performance liquid chromatography (nano-HPLC) coupled with a high resolution Orbitrap LTQ-XL mass spectrometer. The obtained data were analyzed with bioinformatic tools. Apolipoproteins displayed higher association with MC liposome incubated in dynamic conditions so the type of incubation does control the surface properties of nanoparticles that, in turn, is able to entirely change the nature of the biologically active proteins in the corona, and thereby possibly also the biological impacts.

[1] I. Lynch , KA Dawson, . Nano Today 3 (2008) 40-47.

## ELECTROCHEMICAL IMMUNOSYSTEM FOR HEPATITIS A VIRUS DETERMINATION

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Outbreaks of *waterborne diseases* are certainly underestimated due to the lack of adequate programs for the epidemiological surveillance. Current legislation for water, shellfish (EC 2073/2005 EC B53/2004) and plant (EC 2073/2005) does not provide for any limitation due to the presence of Hepatitis A (HAV) and other enteric viruses in the irrigation and housing water. In addition, there is no official method for the detection of these viruses. Currently, the environmental presence of HAV virus is only determined after the outbreak. The diagnosis is based on the patient's symptoms and more specifically through the search for anti-HAV IgM and/or anti-HAV IgG antibodies in blood.

Immunoanalytical approaches are showed as method to determine HAV direct in water, before its use or drinking, thus avoiding the infectious disease.

In this work, two electrochemical, competitive and sandwich, Enzyme Linked ImmunoMagnEtic assays (ELIME) are showed. These systems are based on the use of a new kind of magnetic nanobeads as solid support for the immunochemical chain, and screen printed electrodes as sensing platform. This rapid and low-cost analysis method involve the use of a portable instrument, able to perform measurements directly in the field.

These ELIME assays showed a working range between  $1 \cdot 10^{-2} - 1 \cdot 10^{-10}$  IU/mL (LOD  $1 \cdot 10^{-8}$  IU/ml) and  $1 \cdot 10^{-2} - 1 \cdot 10^{-10}$  IU/ml (LOD  $8 \cdot 10^{-7}$  IU/ml) for competitive and sandwich format, respectively. The proposed systems were applied to drinking water. The results obtained on real samples were compared with those obtained by the qRT-PCR analysis, a routine technique applied by the controllers in evaluating the contamination levels in different samples.

**QUANTITATIVE ANALYSIS OF EPERISONE HYDROCHLORIDE AND PARACETAMOL IN MOUSE PLASMA BY USING HPLC-PDA**

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This work reports the validation of a quantitative HPLC-PDA method for the simultaneous analysis, in mouse plasma, of Eperisone Hydrochloride and Paracetamol. The analytes were resolved on a Gemini C18 column using a gradient elution mode with a run time of 15 minutes, comprising re-equilibration, at 60°C. The method was validated over the concentration range from 0.5 to 25 mg/mL for Eperisone Hydrochloride and Paracetamol, in plasma. Ciprofloxacin was used as Internal Standard.

Results from assay validations show that the method is selective, sensitive and robust. The limit of quantification of the method was 0.5 mg/mL for Eperisone Hydrochloride and Paracetamol, and matrix-matched standard curves showed a good linearity, up to 25 µg/mL with correlation coefficients ( $r^2$ ) 0.9891. In the entire analytical range the intra and inter-day precision (RSD%) values were  $\leq 1.15\%$  and  $\leq 1.46\%$  for Eperisone Hydrochloride, and  $\leq 0.35\%$  and  $\leq 1.65\%$  for Paracetamol. For both analytes the intra and inter-day trueness (Bias%) values ranged, respectively, from  $-5.33\%$  to  $4.00\%$  and from  $-11.4\%$  to  $-4.00\%$ .

The method was successfully tested [1] in pharmacokinetic studies after oral administration in mouse.

[1] M. Locatelli, R. Cifelli, C. Di Legge, R.C. Barbacane, N. Costa, M. Fresta, C. Celia, C. Capolupo, L. Di Marzio, *Journal of Chromatography A* 1388 (2015) 79-86.

## NANOFORMULATIONS OF BERGAMOT ESSENTIAL OIL FOR *IN VITRO* ANTI NEUROBLASTOMA TREATMENT

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Citrus extracts, particularly bergamot essential oil (BEO) and its fractions, have been found to exhibit anticancer efficacy. However, the poor water solubility, low stability and limited bioavailability have prevented the use of BEO in cancer therapy. In order to improve the water solubility of the phytocomponents and increase anticancer activity *in vitro* against human SH-SY5Y neuroblastoma cells were formulated BEO liposomes. Antiproliferative activity of BEO and bergapten-free BEO (BEOBF) loaded in pegylated liposomes were tested and the results demonstrate that the liposomal formulations have increased anticancer activity when compared to the free compound. BEO and BEO-BF were characterized using high performance liquid chromatography (HPLC) and principal parameters were evaluated, as the entrapment efficacy for BEO and BEO-BF, and the liposomal size not only for BEO and BEO-BF but also for empty vesicles.

These results demonstrate that BEO derivatives can perturb the structure of liposomes due to the presence of multiple components, which assemble into a phytocomplex.

[1] C. Celia, E. Trapasso, M. Locatelli, M. Navarra, C.A. Ventura, J. Wolfram, M. Carafa, V.M. Morittu, D. Britti, L. Di Marzio, D. Paolino, *Colloids and Surfaces B: Biointerfaces* 112 (2013) 548-553.



## MEPS-UPLC-PDA ANALYSIS OF NSAIDs DRUGS IN DIALYZED SAMPLES. OPTIMISATION BY RESPONSE SURFACE METHODOLOGY

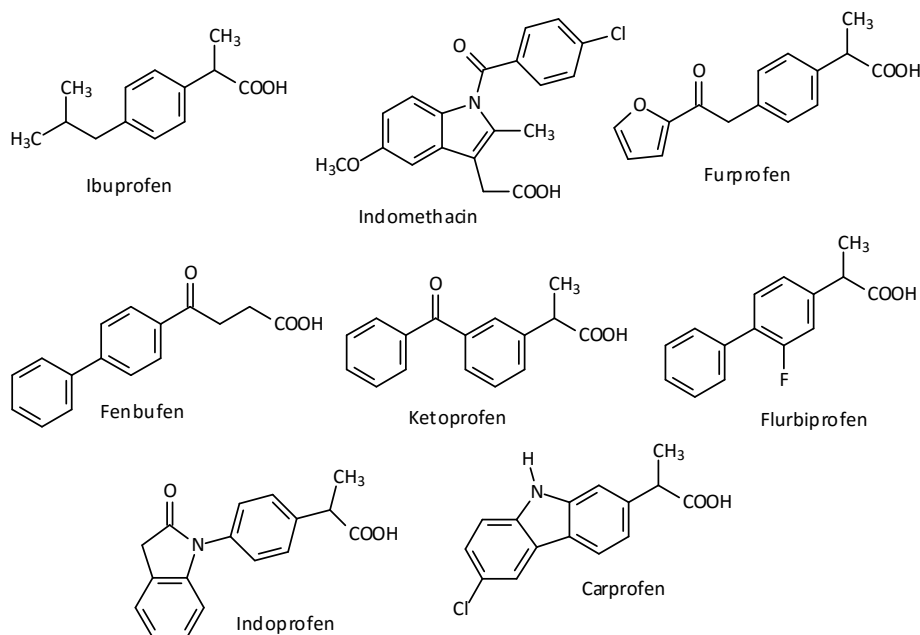
G. Carlucci<sup>1</sup>, A.A. D'Archivio<sup>2</sup>, M.A. Maggi<sup>3</sup>, F. Ruggieri<sup>2</sup>, M. Carlucci<sup>1</sup>, V. Ferrone<sup>1</sup>

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<sup>2</sup>Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila, via Vetoio, 67010 Coppito, L'Aquila,

<sup>3</sup>Hortus Novus, via Collepietro, 67100 L'Aquila,

The optimization of the UPLC-PDA procedures and the investigation of the predictive models are generally seen as distinct tasks although they could be both approached by very similar chemometric methods [1]. In this work a procedure based on microextraction by packed sorbent (MEPS) followed by ultra-performance liquid chromatography (UPLC) with PDA detection has been developed for the analysis of multiple drugs in human dialysate.



The method was applied with good accuracy and precision in the determination of NSAIDs in human dialysate from patients treated with selected drugs.

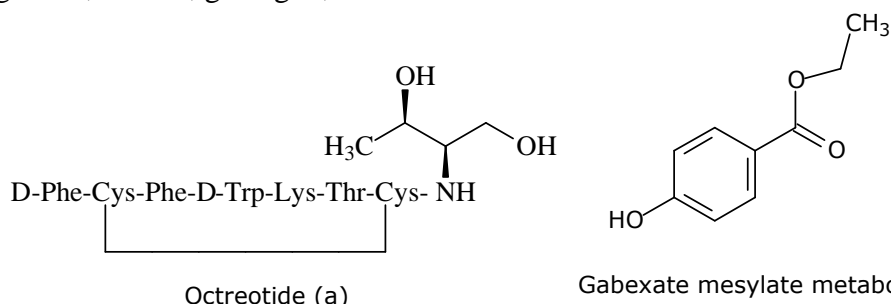
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## OCTREOTIDE AN ANALOG OF SOMATOSTATIN AND GABEXATE MESYLATE IN HUMAN PANCREATIC JUICE SAMPLES MEASURED BY HPLC-DAD-FL DETECTION

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Gabexate mesylate or ethyl-*p*-(6-guanidinohexanoyloxy)benzoate methanesulfonate (a), is a nonantigenic synthetic inhibitor of plasmatic and pancreatic serine proteinases, that is used therapeutically in the treatment of pancreatitis and disseminated intravascular coagulation and as a regional anticoagulant for hemodialysis. Octreotide or [10-(4-aminobutyl)-19-(2-amino-3-phenylpropanoyl)-amino-16-benzyl-N-(1,3-dihydroxy butan-2-yl)-7-(1-hydroxyethyl)-13-(1H-indol-3-ylmethyl)-6,9,12,15,18-pentaoxo-1,2-dithia-5, 8, 11,14,17-pentazacycloicosane-4-carboxamide (b) is a synthetic long-acting cyclic octapeptide, which is a somatostatin analog that has a longer half life and more selectivity in inhibiting hormone secretion than somatostatin [1]. It is used for the clinical management of endocrine disorders where it acts by inhibiting the release of growth, insulin, glucagon, and some other hormones.



This paper reports the validation of a quantitative high performance liquid chromatography-photodiode array-fluorescence (HPLC-PDA-FL) method for the simultaneous analysis of octreotide and gabexate mesylate metabolite in pancreatic juice by protein precipitation using zinc sulphate-methanol-acetonitrile containing the derivatizing reagent, 4-Fluoro-7-nitro-[2,1,3]-benzoxadiazole (NBD-F). Derivatized products of octreotide and gabexate mesylate metabolite were separated on a Luna C<sub>18</sub> column (4.6 mm x 250 mm; 5µm particle size) using a gradient with a run time of 36 min, without further purification. The method was validated over the concentration range of 0.1-15 µg/mL and 0.2-15 µg/mL for octreotide and gabexate mesylate metabolite, respectively, in human pancreatic juice.

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**IDENTIFICATION BY NANO-LC AND TANDEM MASS SPECTROMETRY OF PROTEINS TRAPPED IN SORBENT CARTRIDGES USED FOR COUPLED PLASMA FILTRATION-ADSORPTION TREATMENTS**

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The application of proteomic technologies to renal pathologies has opened new avenues to the dialysis treatments, with specific reference to the development of new biocompatible materials. Recently, coupled plasma filtration adsorption (CPFA) has been proposed as a novel treatment for septic shock to remove inflammatory mediators from blood [1,2]. In order to test the efficacy of cartridge resins used for CPFA, analytical methods for profiling plasma proteins trapped in the sorbent resins are highly desirable. In this work, the identification of proteins trapped into sorbent resin cartridges used for coupled plasma filtration-adsorption of healthy and septic pigs has been performed by liquid chromatography (LC) coupled to mass spectrometry (MS). The five main steps of the proteomics analysis, (i) protein extraction from cartridge resins, (ii) two-dimensional gel electrophoresis, 2-DE, for protein separation, (iii) in-gel proteolytic digestion, (iv) tandem mass analysis of peptides resulting from enzymatic cleavage and (v) bioinformatics, for protein identification and characterization, have been carefully optimized. The efficiency of different extraction solutions and procedures for protein recovery from sorbent resins were critically evaluated. Then, a simple method for high-throughput protein identification, using gradient LC elution into an ion trap mass spectrometer was developed. The nanoLC-ESI-ITMS/MS method was tailored for detecting and sequencing the highest number of peptides from a single analysis, by using few microlitres of the enzymatically hydrolyzed protein extract. The objective of our study was to obtain a reference map of plasma proteins trapped into sorbents for CPFA, which is an essential step for designing new bio-filters to be used in dialysis treatments. The described procedure represents the first step for plasma protein profiling and for designing new bio-filters able to control the inflammatory imbalance.

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**DIRECTING SUPRAMOLECULAR ASSEMBLY AT INTERFACES:  
FROM FUNCTIONAL NANOMATERIALS TO IMAGING PROBES FOR  
BIOLOGICAL SYSTEMS**

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The ability to carry out a remarkable array of complex functions using molecular self-assemblies is one of the fundamental features of biological systems. A key consideration in molecular surface recognition of proteins is the modulation of noncovalent forces on the sub-nanometer scale on the protein surface to allow high efficiency and specific recognition capabilities. Inspired by the beauty and complexity of Nature, it is possible to develop molecular systems for the recognition and self-assembly of building blocks by the manipulation of noncovalent interaction within defined molecular architecture on surfaces. The ability to tailor the physical, chemical and biological properties at the interface of nanostructured materials by surface assembling of functional molecules [1] paves the way for the investigation of more sophisticated processes. Since the robust structure and unique properties, carbon based nanomaterials have emerged as one of the most promising classes of scaffold nanostructures for the investigation in the biological setting. By embracing the concepts learned in the study of supramolecular organization processes with the properties of material at the nanoscale, our research work has allowed not only the development of novel strategies to efficiently prepare functional nanomaterials [2], but it helps to investigate their behaviour at the cellular interface, which could make it possible in the future to reveal underlying principle of biological systems. The development of methods to realize biomimetic surfaces by expanding the role of noncovalent interactions at the interface exhibiting high affinity and selectivity toward a range of biomolecules and biomarkers in general, represents a powerful tool for the generation of analytical platforms with important implication in diagnostic.

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**DIFFERENCES IN SALIVARY ALPHA-AMYLASE AND CORTISOL RESPONSIVENESS OF PSORIATIC PATIENTS UNDERGOING THE TRIER SOCIAL STRESS TEST**

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Psoriasis is a chronic and inflammatory skin disease (2-3% prevalence in the population) characterised by a significant psychological distress and psychiatric morbidity, experiences of stigmatization, and decreased quality of life [1]. The etiology of psoriasis is not fully understood but it appears to have a multifactorial character, involving both genetic and environmental influences. Among possible factors, the emotional stress is thought to play an important role both in the onset and in the exacerbation of the disease [2-3]. In response to a stressor, two major biological systems are activated, i.e. the Autonomic Nervous System (ANS), indexed by a salivary alpha amylase (sAA) [4], and the Hypothalamic-Pituitary-Adrenal (HPA) axis, whose main biomarker of activation is represented by cortisol [5].

sAA is an enzyme produced in the mucosa of salivary glands in response to the activation of neurotransmitters, whereas cortisol is a lipophilic steroid hormone produced in the zona fasciculata of the adrenal gland. Only 5-10% of the circulating cortisol is unbound and free to accomplish its biological action, and this fraction passively diffuses towards the saliva via ultra-filtration. Cortisol levels measured in saliva agree very well with the amount of free cortisol in blood [6].

This study was designed to determine the cortisol and sAA levels in saliva and to investigate the responses of the two primary neuroendocrine systems (the HPA and ANS systems) in psoriatic volunteers after the administration of a psychosocial stress test (the Trier Social Stress Test, TSST).

Saliva is a readily available specimen offering potential advantages in terms of a non-invasive and stress free sample collection as well as simple sample treatment. In our study, the analytical procedures for the sampling of saliva and the determination of sAA and cortisol levels were developed and optimised. sAA was measured by a colorimetric method based on an enzymatic reaction with a cross-linked starch polymer bearing a chemically bound blue dye, followed by UV-vis spectrophotometric detection. The determination of salivary cortisol was carried out by Reversed-Phase High-Performance Liquid Chromatography coupled to Electrospray Ionization Quadrupole Time-of-Flight Mass Spectrometry (RP-

HPLC-ESI-Q-ToF). The determination of the salivary levels of these analytes could offer an alternative approach to investigate the responsiveness of psoriatic patients to stressors, thus allowing a better understanding of the possible role of stress in the etiology or exacerbation of disease and the possible identification of patients who could benefit from an additional psychological therapy.

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**INFLUENCE OF THE SAMPLING PROCEDURE ON THE MEASURED CONCENTRATION OF URIC ACID IN ORAL FLUID**

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Uric acid (UA), a weak acid ( $pK_a = 5.4$ ) distributed throughout the extracellular fluid compartment as sodium urate, is the final oxidation product of the catabolism of purine nucleotides in humans and is excreted in urine. The non-invasive measurement of uric acid in oral fluid may be a useful tool for monitoring patients affected by gout, hypertension, cardiovascular and neurodegenerative diseases due to its role in the pathogenetic mechanism of such diseases.

In this work, the influence of sampling parameters such as oral fluid pH and flow rate on the concentrations of UA in oral fluid (OF) was evaluated. Samples of non-stimulated and stimulated OF were collected from 10 healthy volunteers using a biocompatible roll-shaped polyester Salivette swab. In particular, the non-stimulated OF samples were collected by asking the subjects to place the swab in the mouth, between the gum and cheek, and to keep it steady for 5 min (no chewing or movements), whereas the stimulated OF samples were collected by rolling a swab into the mouth for 1 min at different frequencies (50, 100 and 150 chew movements/min).

The amount of the absorbed OF sample was calculated according to weight differences before and after sampling. From these values, the OF flow rate in mL per minute was calculated. After OF sampling, the pH was measured by two independent observers using a narrow range (resolution of 0.3 pH units) pH paper strip (Pehanon, Macherey Nagel). The OF was recovered by centrifugation of the swabs at 3000 rpm for 5 min at room temperature.

After a 50-fold dilution with the mobile phase (3% acetonitrile and 97% water with 0.1% of formic acid), the UA concentration in OF samples was measured by HPLC-UV. The chromatographic separation was carried out in isocratic conditions using a Zorbax SB-Aq reversed-phase column, and ultraviolet detection was performed at 290 nm.

Results highlight that the concentration of uric acid in oral fluid is not influenced by pH and is inversely proportional to flow rate. Since uric acid does not diffuse through the salivary membrane due to its low hydrophobicity, a transfer process probably mediated by the membrane carrier URAT1 was hypothesized.

## **USING MS<sup>E</sup> AS A NEW TOOL FOR QUANTIFICATION IN A GLP REGULATED ASSAY VALIDATION FACILITY.**

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The objective of this work is to present the validation of a LC-MS (UPLC-QTOF) computerised system in a GLP Assay Validation Facility and the related analytical Performance Qualification (PQ) procedure using a new analysis type (MS<sup>E</sup>) approach for quantification.

The approach consisted in a quantification method of a small molecule (1' Hydroxymidazolam) using MS<sup>E</sup> technique and a software created for regulated bio analytics environment.

The idea is use to the mass spectrometer type well known for metabolite identification also for quantification of known metabolites e.g for test system characterization for phase I and phase II regarding metabolic competence in biotransformation.

Quadrupole –time-of-flight mass spectrometers have rapidly embraced by the analytical community as powerful and robust instruments able to combine the high performance of time-of-flight analyses in MS and MS/MS modes with the accepted ESI and APCI techniques of ionization. Originally targeted for peptides analysis we are focused on small molecules analysis in biological samples using the combination of high sensitivity and high mass accuracy for both precursor and product ions.

The new MS<sup>E</sup> method will be also applied for an analyte cocktail approach to obtain fragmentation information by doing simultaneous acquisitions of exact masses at high and low collision energies.

Using this new analysis type parallel alternating scans are acquired at either low collision energy in the collision cell to obtain precursor information or high collision energy to obtain full scan accurate mass fragment, precursor ion and neutral loss information. All of this data are obtained from a single analytical run.

This system approach fulfils chromatographic and MS efficiencies for the task of structural elucidation and quantification in complex mixtures as required in regulated environment.

Raw data and criteria chosen for the PQ will be shown.

Standards did not deviate by more than 15% of nominal concentrations; Lower Limit of Quantification (LLOQ) did not deviate by more than 20%.

The acceptance criteria for the standards curve met the above criteria, including the LLOQ and Upper Limit of Quantification (ULOQ) and no points of the curve were not excluded. Accuracy and precision were determined by replicate analysis of samples containing known amounts of the analyte as quality controls (QC) (in this case LLOQ, QC-L, QC-M, QC-H) and were measured using five



determinations per concentration. For the accuracy the mean value was within 15% of the nominal value except at LLOQ, where it didn't deviate by more than 20%. The precision determined at each concentration level didn't exceed 15% of the coefficient of variation (CV) except for the LLOQ, where it did not exceed 20% of the CV. Carry over in the blank sample following the high concentration standard were lower than 20% of the lower limit of quantification (LLOQ) and 5% for the internal standard.

Spectra and chromatograms will be elucidated and described.

In conclusion the MS<sup>E</sup> approach can generate both precursor and product ions in a single analytical run thereby eliminating the need to rerun the samples to obtain further MS/MS spectra. The relevant precursor and product ion are linked using retention times, mass defect or a combination of both. As results it is possible to have good values of linearity, accuracy and precision and using an interactive workflow-driven data platform for comprehensive reporting, that enables routine deployment in a GLP regulated assay validation facility.

**THE MONITORING OF OCCUPATIONAL EXPOSURE TO ACTIVE PHARMACEUTICAL INGREDIENTS: DETERMINATION OF CHEMICAL TRACERS ON MEMBRANE FILTERS BY NIR/PLS METHOD**

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The supervision of work environments through monitoring of analytes that provoke occupational disease holds great interest. From the analytical point of view, the focus is shifting increasingly on economic, rapid, sensitive, and if possible, user-friendly methods.

Near infrared spectroscopy (NIRS) associated with multivariate analysis is a fast, non-destructive technique that allows direct analysis on several complex matrices. It would satisfy the requirements to obtain data in real time in case of acute accidental exposure to workers. Therefore it could represent an innovative and particularly suitable analytical tool. Many NIRS applications can be found in the pharmaceutical field [1]. In this way the new technique could be easily accepted as an alternative method, for the control of environmental quality in the pharmaceutical production laboratory [2].

The potential of this approach has been evaluated in terms of quantitative determination of lactose, mannitol and sucrose directly on air sampling filters. The excipients are generally employed as chemical tracers for the evaluation of exposure risk to active pharmaceutical ingredients.

The laboratory training set was obtained sampling filters inside a glove box in order to reproduce typical controlled conditions of a production laboratory. A number of different spectral pre-processing techniques were applied to optimize partial least squares regression (PLSR) models on NIRS data. Standard normal variate (SNV) and Savitsky-Golay derivatives allowed to control the inter and intra-filter variability. The optimal PLS model for lactose produced a root mean square error of calibration (RMSEC) of 0.99 ng, the RMSECV in cross-validation of 1.67 ng and the RMSEP in prediction of 1.92 ng. The model was tested on a limited prediction set composed of real filters giving a RMSEP of 2 ng. The results using new technique compare favourably with the limit of quantification (LOQ) of 12 ng obtained with the reference method UPLC/MS.

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**TOTAL CONCENTRATION AND BIOACCESSIBILITY OF POTENTIALLY TOXIC ELEMENTS IN AYURVEDIC FORMULATIONS**A. Giacomino<sup>1</sup>, M. Malandrino<sup>2</sup>, C. La Gioia<sup>2</sup>, E. Magi<sup>3</sup>, O. Abollino<sup>2</sup><sup>1</sup>Dipartimento di Scienze e Tecnologia del Farmaco, Università di Torino, Via Giuria 9, 10125 Torino<sup>2</sup>Dipartimento di Chimica, Università di Torino, Via Giuria, 10125 Torino<sup>3</sup>Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, 16146 Genova

Some metal-based preparations used in the ayurvedic medicine, an Indian system of medicine, have been suspected to be harmful because some patients were poisoned by heavy metals after the ingestion of these remedies [1]. On the other hand, ayurvedic medicines are being used by millions of people in India without apparent side effects. For these reasons it is interesting to determine the element content in ayurvedic medicines, taking into account that they are increasingly consumed also Western countries. Moreover, the total concentration of an element is not sufficient to assess its potential harmful effects, since not all the amount present in an ingested product is available for absorption by the organism; for this reason, it is useful to determine the amount assimilated after ingestion. This can be estimated *in vitro* by measuring the bioaccessibility, i.e. the fraction of a compound that is released from its matrix in the gastrointestinal tract.

In this work we have determined the total concentrations of 25 elements in 17 ayurvedic products sold in different distribution channels: Indian ayurvedic medical shops, an Italian pharmacy and on the Internet. Metal bioaccessibility was studied by extraction with solutions simulating gastric and intestinal fluids. Concentrations were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Five medicines purchased in India contained very high total amounts of As, Cu, Hg, and Pb and two products had bioaccessible As concentrations greater than the corresponding maximum admissible daily intake level. Concentrations in the products purchased on the Internet and in the Italian pharmacy were lower than the safety limits fixed by the international authorities.

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## **IDENTIFICATION AND CHARACTERIZATION OF NEW BIOACTIVE PEPTIDES IN DONKEY MILK SAMPLES**

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Donkey milk is an interesting commercial product for its nutritional values, which make it the most suitable mammalian milk for human consumption, and for the bioactivity associated with it and derivative products.

Donkey milk is a rich source of endogenous bioactive peptides of great interest for their healthy properties.

To further mine the characterization of donkey milk, an extensive peptidomic study was performed. Naturally occurring peptides were first purified by precipitation with an organic solvent, such as cold acetone.

Since peptides with a chain length 7-20 AAs or with a MW <700-2000 Da, are usually the most active, we decided to use ultrafiltration membrane systems to separate peptides with desired molecular weights.

In order to select <2000 Da molecules, the extracts were either ultrafiltered with 2 mW cut-off. The isolated peptides were subjected to *in vitro* bioactivity assays, in particular one bioactivity was considered, namely the angiotensin converting enzyme (ACE).

The extracts were further fractionated on semi-preparative scale using a polymeric reversed phase (C18 silica, 5 $\mu$ m) column.

The peptides were subjected again to *in vitro* bioactivity assays to assess the bioactivity of the single isolated fractions. Based on bioactivity assay, extract fractions were further selected for analysis by nanoHPLC with direct injection into a Orbitrap mass spectrometer for peptide sequencing.

Bioinformatic tools for analysis and identification of peptides from MS/MS spectra were employed. The MS/MS spectra were subject to database search by a search engine, able to compare the amino acidic sequences of the analyzed peptides with those obtained from *in-silico* digestion of proteins contained in the database. Since donkey is not an organism the sequence of which is completely sequenced, the bioinformatics analysis of the acquired MS/MS spectra were also performed by *de novo* sequencing,

Moreover, the data were refined and completed by another bioinformatics analysis, this time aimed at predicting the possible biological activity based on the analogy to known bioactive peptides or specific sequence patterns.

The developed protocol provided an analytical platform for the comprehensive description of the peptide profile in donkey milk samples.

## PROTEOME ANALYSIS OF SOYBEAN EMBRYONIC AXES UNDER SALT STRESS

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Salinity is one of the major abiotic stresses affecting crops. High salt concentrations have negative impacts on germination, growth, nodulation, seed quality and quantity, thus reducing the yield of production [1,2]. For this reason, there is great interest in understanding the genetic basis of salinity tolerance and adaptation mechanisms.

Soybean (*Glycine max* (L.) Merrill), the world’s most important food legume, provides an inexpensive source of protein and edible oil for human consumption. In addition soybean seeds have the ability to germinate even under high salinity, even if this condition lowers the yield [3]. This ability makes it an appropriate model for elucidating the salt-stress-responsive proteins and their corresponding genes in this species.

For this purpose, a comparative label-free quantitative proteomic analysis of embryonic axes during germination *sensu stricto* (GSS) under saline and non-saline conditions was performed. A total of 15644 peptides were identified and quantified, with 9187 of them being unique peptides, corresponding to 1710 non-redundant proteins at a FDR of 1%. As revealed by nanoliquid chromatography-tandem mass spectrometry, the application of 100 and 200 mmol L<sup>-1</sup> NaCl at GSS was significantly accompanied by the change in abundance (>2-fold) of 97 and 75 proteins, respectively. Most of these proteins are involved in four major functions, namely stress related-proteins, protein turnover and protection, primary metabolism and energy, and signal transduction. Overall, our results indicate that the cross-protection against aldehydes, oxidative as well as osmotic stress is the major adaptive response to cope with high salinity.

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