Divisione di Chimica Analitica
Società Chimica Italiana

Università degli Studi di Genova

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

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XXIV Congresso della Divisione di Chimica Analitica della SCI

Sestri Levante, 15-19 Settembre 2013

Domenica 15 Settembre 2013

16.00-19.00 Registrazione dei partecipanti
19.30-21.00 Cocktail di benvenuto

Lunedì 16 Settembre 2013

Sessione Plenaria 1
SALA AGAVE

9.00-9.45 Apertura del Congresso
PRESIEDE: **Giuseppe Arena**
9.45-10.30 **Conferenza Plenaria 1**
PL01 NEURAL INTERFACES: FROM HYBRID CHIPS TO NEURAL PROSTHESIS
Fabio Benfenati
Department of Neuroscience and Brain Technologies, Fondazione Istituto Italiano di Tecnologia (IIT); Department of Experimental Medicine, University of Genova.

Sessione Parallela 1a: Bioanalitica e Omics
SALA AGAVE

PRESIEDE: **Aldo Roda**
10.30-10.50 **O01** OFET DEVICES: A NEW STRATEGY FOR LABEL-FREE ELECTRONIC BIOSENSORS DEVELOPMENT
M. Magliulo[1], K. Manoli[1], E. Macchia[3], F. Giordano[3], A. Mallardi[2], G. Palazzo[1], Luisa Torsi[1]
[1]Dipartimento di Chimica - Università degli Studi di Bari
[2]CNR-IPCF, Istituto per i Processi Chimico-Fisici – Bari
[3]Dipartimento di Fisica - Università degli Studi di Bari
10.50-11.10 **O02** THERMODYNAMIC BASIS FOR ENGINEERING HIGH AFFINITY AND HIGH SPECIFICITY BINDING-INDUCED CLAMP SWITCHES
A. Idili[1], A. Vallée-Bélisle[2], K.W. Plaxco[3], G. Palleschi[1], Francesco Ricci[1]
[1]Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata
[2]Laboratory of Biosensors and Nanomachines, Université de Montréal, Canada
[3]Department of Chemistry and Biochemistry and Interdepartmental Program in Biomolecular Science and Engineering, University of California, USA

11.10-11.40 ***Coffee break***

PRESIEDE: **Giovanni Sindona**

11.40-12.00 **O03** SURFACE PLASMON RESONANCE IMAGING AND HUMAN DNA: HIGH SENSITIVE DETECTION AND POLYMORPHISM DISCRIMINATION
Stefano Mariani[1], M.L. Ermini[1], S. Scarano[1], R. Barale[2], M. Minunni[1]
[1]Dipartimento di Chimica, Università degli Studi di Firenze
[2]Dipartimento di Biologia, Università, degli Studi di Pisa

12.00-12.20 **O04** ENHANCING THE SENSITIVITY OF LATERAL FLOW IMMUNOASSAY WITH SILVER NANOPARTICLE AND FLUORESCENT SEMICONDUCTOR NANOCRYSTAL (QUANTUM DOTS) PROBES
Laura Anfossi[1], C. Giovannoli[1], C. Passini[1], C. Baggiani[1], I.Y. Goryacheva[2], E.S. Speranskaya[2]
[1]Dipartimento di Chimica, Università di Torino
[2]Chemistry Department, Saratov State University, Russia

12.20-12.40 **O05** NEW ACRIDINE-CONTAINING 1,2-DIOXETANE DERIVATIVES AS PROMISING THERMOCHEMILUMINESCENT LABELS FOR BIOANALYTICAL APPLICATIONS
Massimo Di Fusco,[1] M. Mirasoli,[2] M. Guardigli,[2] A. Quintavalla,[2] M. Lombardo,[2] C. Trombini,[2] A. Roda[2]
[1]Advanced Applications in Mechanical Engineering and Materials Technology Interdepartmental Center for Industrial Research, University of Bologna
[2]Department of Chemistry, University of Bologna

12.40-13.00 **O06** NEW APTASENSORS FOR EARLY DIAGNOSIS OF BREAST CANCER
Andrea Ravalli, G. Marrazza
Dipartimento di Chimica, Università di Firenze

Sessione Parallela 1b: Scienza delle Separazioni
SALA OLEANDRO

PRESIEDE: **Luigi Mondello**

10.30-10.50 **O07** SEPARATION AND QUANTIFICATION OF PLANT SECONDARY METABOLITES AND OTHER BIOLOGICAL MOLECULES BY ADVANCED ANALYTICAL SEPARATION METHODS
Danilo Corradini, I. Nicoletti
Institute of Chemical Methodologies, CNR, Area della Ricerca di Roma 1, Montelibretti, Monterotondo Stazione (Rome)

10.50-11.10 **O08** INNOVATIVE CAPILLARY ELECTROPHORESIS METHOD DEVELOPMENT FOR THE DETERMINATION OF ALMOTRIPTAN AND ITS IMPURITIES: QUALITY BY DESIGN APPROACH
Sandra Furlanetto, S. Orlandini, B. Pasquini, S. Pinzauti
Dipartimento di Chimica, Università di Firenze

11.10-11.40 ***Coffee break***

PRESIEDE: **Danilo Corradini**

11.40-12.00 **O09** ON-LINE SPE-LC-MS/MS ANALYSIS OF SELECTED ENDOCRINE DISRUPTOR COMPOUNDS (EDCs) IN SURFACE WATER AND WASTEWATER SAMPLES IN ITALY
Lorenzo Ciofi, M. Del Bubba, C. Ancillotti, L. Checchini
Department of Chemistry, University of Florence

12.00-12.20 **O10** MOLECULARLY IMPRINTED BEADS FROM SACRIFICIAL POROUS SILICA: SYNTHESIS, PROPERTIES AND ANALYTICAL APPLICATIONS
Cristina Giovannoli, C. Passini, L. Anfossi, G. Magnacca, C. Baggiani
Dipartimento di Chimica, Università di Torino

12.20-12.40 **O11** GAS CHROMATOGRAPHIC APPROACHES FOR THE DETERMINATION OF NEW MARKERS OF CELLULOSE DEGRADATION IN INSULATING MINERAL OILS OF POWER TRANSFORMERS
Rosa Maria De Carlo[1], M.C. Bruzzoniti[1], C. Sarzanini[1], R. Maina[2], V. Tumiatti[2]
[1]University of Torino, Department of Chemistry
[2]Sea Marconi Technologies, Collegno (Torino)

12.40-13.00 **O12** HEADSPACE SOLID-PHASE MICRO-EXTRACTION ANALYSIS OF SHORT CHAIN FATTY ACIDS IN FAECAL SAMPLES: APPLICATION TO COMPARATIVE METABOLOMIC STUDIES OF THE HUMAN GUT MICROBIOTA
Giulia Basaglia[1], M. Centanni[2], J. Fiori[1,2], S. Rampelli[2], S. Turroni[2], E. Biagi[2], M. Candela[2], P.Brigidi[2], R. Gotti[1,2]
[1]Interdepartmental Center for Industrial Research – Advanced Mechanical and Materials, University of Bologna
[2]Department of Pharmacy and Biotechnology, University of Bologna

13.00-14.30 ***Pranzo***

14.30-15.30 **Sessione poster 1**

Sessione Parallela 1c: Bioanalitica e Omics
SALA AGAVE

PRESIEDE: **Claudio Baggiani**

15.30-15.50 **O13** DETERMINATION OF ANTICOAGULANT DRUGS AND THEIR METABOLITES IN ORAL FLUID AND PLASMA SAMPLES BY HPLC-FLUORIMETRY
Silvia Ghimenti[1], R. Fuoco[1], T. Lomonaco[1], I. Piga[1], D. Biagini[1], M. Onor[2], A. Paolicchi[3], L. Ruocco[4], G. Pellegrini[4], M. G. Trivella[5], F. Di Francesco[1,5].
[1]Department of Chemistry and Industrial Chemistry, University of Pisa
[2]Institute of Chemistry of Organometallic Compounds, CNR, Pisa
[3]Department of Translational Research and New Technologies in Medicine and Surgery, University of Pisa
[4]Chemical-Clinical Analysis Laboratory, AOUP, Pisa
[5]Institute of Clinical Physiology, CNR, Pisa

15.50-16.10 **O14** ELECTROCHEMICAL IMMUNOASSAY FOR SCREENING OF CELIAC DISEASE IN SALIVA

G. Adornetto[1], L. Fabiani[1], G. Volpe[1], A. De Stefano[1], S. Martini[2], G. Gallucci[2], F. Lucantoni[3], C. Tiberti[3], M. Bonamico[3], Danila Moscone[2]

[1]Dipartimento di Scienze e Tecnologie Chimiche, Università Tor Vergata, Roma

[2]RADIM SpA, Pomezia RM

[3]Dipartimento di Pediatria, Università di Roma La Sapienza

16.10-16.30 **O15** HUMAN BLOOD MICROPARTICLES AND PLATELETS: A COMPARATIVE PHOSPHOLIPIDOMIC INVESTIGATION BY HYDROPHYLIC INTERACTION LIQUID CHROMATOGRAPHY-ELECTROSPRAY IONIZATION MASS SPECTROMETRY

Ilario Losito[1,2], R. Patruno[1], E. Conte[3], T.R.I. Cataldi[1,2], N. Cioffi[1], F.M. Megli[3], F. Palmisano[1,2]

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[3]Dipartimento di Biochimica e Biologia Molecolare, Università degli Studi di Bari

16.30-17.00 ***Coffee break***

PRESIEDE: **Mauro Tomassetti**

17.00-17.20 **O16** INTERACTION BETWEEN TREHALOSE CONJUGATED β-SHEETBREAKER PEPTIDE AND Aβ(1-42) MONOMERS: INSIGHT INTO THE Aβ RECOGNITION PROCESS AND NEUROPROTECTION

Alessandro Giuffrida[1], F. Attanasio[1], I. Naletova[3], M.L. Giuffrida[1], A. Sinopoli[4], G. Pappalardo[1], E. Rizzarelli[1,2]

[1]CNR-Institute of Biostructure and Bioimaging, Catania

[2]University of Catania, Department of Chemical Sciences

[3]University of Catania, Department of Biomedical Sciences

[4]University of Catania, International PhD Program in Translational Biomedicine, University of Catania

17.20-17.40 **O17** ANALYTICAL PLATFORM FOR THE PROTEOME ANALYSIS OF NON MODEL PLANT SPECIES

Anna Laura Capriotti, V. Colapicchioni, S. Piovesana, R. Samperi, A.Laganà

Dipartimento di Chimica, Sapienza Università di Roma

17.40-18.00 **O18** PROTEIN LABBELING BY P-HYDROXYMERCURYBENZOATE: A LOW COST PROTEOMICS.

Beatrice Campanella[1], M. Onor[1], A. D'Ulivo[1], J. González Rivera[2], C. Ferrari[3], S. Giannarelli[4], E. Bramanti[1]

[1]C.N.R., Institute of Chemistry of Organometallic Compounds, Pisa

[2]Chemical Engineering Department, University of Guanajuato, Mexico.

[3]C.N.R., Istituto Nazionale di Ottica, INO –Pisa

[4]Dept. of Chemistry and Industrial Chemistry, University of Pisa

Sessione Parallela 1d: Beni Culturali

SALA OLEANDRO

PRESIEDE: **Luigia Sabbatini**

15-30-15.50 **O19** ASSESSMENT OF INNOVATIVE TECHNIQUES FOR RESTORATION

C. Berlangieri[1], F. Demeo, Emiliano Carretti[1], C. Matarrese[1], M. Severi[1], R. Traversi[1], R. Udisti[1], L. Dei[1], P. Baglioni[1].

[1]Department of Chemistry & CSGI Consortium University of Florence

15.50-16.10 **O20** IRON GALL INKS: IS COPPER A KEY ELEMENT FOR HISTORICAL AND ARCHAEOMETRIC INFORMATION ON MEDIOEVAL MANUSCRIPTS? AN APPLIED RESEARCH FOCUSED ON GUARNERIO D'ARTEGNA (1410-1466)

Gianpiero Adami[1], M. Crosera[1], P. Barbieri[1], C. Federici[2], A. Giacomello[3]

[1]Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste

[2]Dipartimento di Studi Umanistici, Università Ca' Foscari di Venezia

[3]Regione Autonoma Friuli Venezia Giulia - Centro Regionale di Catalogazione e Restauro dei Beni Culturali - Passariano (UD)

16.10-16.30 **O21** USE OF NANO GOLD PARTICLES OBTAINED BY LASiS FOR SEIRA AND IMMUNO-SERS ANALYSES OF HERITAGE MATERIALS

Giorgia Sciutto[1], S. Prati[1], R. Mazzeo[1], A. Roda[2], L. Litti[3], M. Meneghetti[3], C. Lofrumento[4], M. Ricci[4], E. Castellucci[4]

[1]Microchemistry and Microscopy Art Diagnostic Laboratory, University of Bologna, Ravenna Campus

[2]Department of Chemistry University of Bologna

[3]Department of Chemical Sciences, University of Padova

[4]Department of Chemistry, Polo Scientifico e Tecnologico, University of Firenze

16.30-17.00 ***Coffee break***

PRESIEDE: **Carlo Dossi**

17.00-17.20 **O22** THE CHEMISTRY OF POLYSACCHARIDE GUMS USED AS PAINT BINDERS: ANALYTICAL PROCEDURES, INTERACTIONS AND AGEING

A. Lluveras-Tenorio[1], J. Mazurek[2], C. Duce[3], M.P. Colombini[3], M.R. Tiné[3], Ilaria Bonaduce[3]

[1]Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Firenze

[2]Getty Conservation Istitute, Los Angeles, USA

[3]Dipartimento di Chimica e Chimica Industriale, Università di Pisa

17.20-17.40 **O23** ELECTROCHEMICAL ANALYSIS OF IMMUNOGLOBULIN-Y WITH ENSEMBLES OF NANOELECTRODES: DETECTION OF EGG-YOLK AS BINDER IN TEMPERA PAINTINGS

F. Bottari[1], P. Oliveri[2], Paolo Ugo[1]

[1]Dipartimento Sc. Molecolari e Nanosistemi., Università Cà Foscari Venezia

[2]Dipartimento di Farmacia, Università di Genova

17.40-18.00 **O24** DEVELOPMENT OF INNOVATIVE EMBEDDING PROCEDURES FOR THE ANALYSES OF PAINT CROSS SECTIONS IN FITR MICROSCOPY

Silvia Prati[1], G. Sciutto[1], E. Catelli[1], F. Rosi[2-3], C. Miliani[2-3], R. Mazzeo[1]

[1]University of Bologna - Ravenna Campus, Microchemistry and Microscopy Art Diagnostic Laboratory (M2ADL)

[2]CNR-ISTM c/o Dipartimento di Chimica Università degli studi di Perugia

[3]Centro SMAArt c/o Dipartimento di Chimica Università degli studi di Perugia

18:15 **Assemblea della Divisione** con consegna dei Premi e delle Medaglie della Divisione (Medaglia Canneri, Medaglia Liberti, Premio Giovane Ricercatore, Premio di Laurea)

Martedì 17 Settembre 2013

Sessione Plenaria 2
SALA AGAVE

PRESIEDE: **Silvia Lanteri**

9.00-9.45 **Sessione Plenaria 2**
PL02 ANALYTICAL CHEMISTRY BEYOND CHEMICAL ANALYSIS
Lutgarde Buydens
Radboud University Nijmegen, Institute for Molecules and Materials, Analytical Chemistry, Chemometrics; Heijendaalse weg 135, 6525AJ Nijmegen, The Netherlands.

Sessione Parallela 2a: Chemiometria
SALA AGAVE

PRESIEDE: **Alessandro Ulrici**

10.00-10.20 **O25** GEOGRAPHICAL TRACEABILITY AND AUTHENTICITY OF EXTRA VIRGIN OLIVE OIL BY CHEMOMETRIC TECHNIQUES AND CHROMATOGRAPHIC FINGERPRINT
Riccardo Nescatelli, R. Bonanni, R. Bucci, A. Magrì, A. Magrì, F. Marini
Dipartimento di Chimica, Università di Roma La Sapienza

10.20-10.40 **O26** DATA FUSION APPROACH FOR THE VARIETAL CLASSIFICATION OF LAMBRUSCO P.D.O. WINES
Marina Cocchi[1], M. Silvestri[1], E. Salvatore[1], A. Elia[1], C. Durante[1], A. Marchetti[1], G. Papotti[2], D. Bertelli[2], M. Plessi[2]
[1]University of Modena and Reggio Emilia, Department of Chemical and Geological Sciences
[2]University of Modena and Reggio Emilia, Department of Life Sciences

10.40-11.00 **O27** KERNEL-BASED BATCH MULTIVARIATE STATISTICAL PROCESS MONITORING: BETTER DISCRIMINATION WITH A BETTER UNDERSTANDING
Raffaele Vitale[1], O.E. de Noord[2], A. Ferrer[1]
[1]Department of Applied Statistics, Operational Research and Quality, Universidad Politécnica de Valencia, Spain
[2]Shell Global Solutions International B.V., Shell Technology Centre Amsterdam, The Netherlands

11.00-11.30 ***Coffee break***

PRESIEDE: **Desimoni Elio**

11.30-11.50 **O28** DATA REDUCTION OF HYPERSPECTRAL IMAGES
Carlotta Ferrari, G. Foca, A. Ulrici
Dipartimento di Scienze della Vita, Università di Modena e Reggio Emilia

11.50-12.10 **O29** USE OF NIR AND PLS IN QUALITY CONTROL OF CARBOXYMETHYLCELLULOSE
Riccardo Leardi[1] , G. Polotti[2] , S. Perelli[3]
[1]Dipartimento di Farmacia, Università di Genova,
[2]Lamberti S.p.A.
[3]Politecnico di Milano

12.10-12.30 **O30** NEW TOOLS FOR DATA PRE-TREATMENT IN LC-MS-BASED METABOLOMICS
Matteo Stocchero
S-IN Soluzioni Informatiche, Vicenza

Sessione Parallela 2b: Equilibri in soluzione e speciazione
SALA OLEANDRO

PRESIEDE: **Pier Giuseppe Daniele**

10.00-10.20 **O31** FLUORESCENCE SENSING AND CELLULAR IMAGING OF Cu^{2+} BY A NEW WATER SOLUBLE CHEMOSENSOR
G.I. Grasso[1], Carmelo Sgarlata[2], C. Satriano[2], M.L. Giuffrida[1], S. Gentile[2], G. Tomaselli[2], L. Prodi[3], G. Arena[2]
[1]CNR - IBB, UOS Catania, Dipartimento di Scienze Chimiche, Università degli Studi di Catania
[2]Dipartimento di Scienze Chimiche, Università degli Studi di Catania
[3]Dipartimento di Chimica, Università degli Studi di Bologna

10.20-10.40 **O32** BINDING ABILITY OF PHOSPHONIC NTA DERIVATIVES TOWARD BIOLOGICALLY AND ENVIRONMENTALLY RELEVANT METAL AND ORGANOMETAL CATIONS
C. Bretti, C. De Stefano, C. Foti, Demetrio Milea
Dipartimento di Scienze Chimiche, Università di Messina

10.40-11.00 **O33** SURFACE CHEMICAL PROPERTIES OF TETRALKYL-AMMONIUM CARBOXYLATES
Gaetano De Tommaso, M. Iuliano, M.C. Sorice
Dipartimento di Scienze Chimiche, Università di Napoli "Federico II"

11.00-11.30 ***Coffee break***

PRESIEDE: **Concetta De Stefano**

11.30-11.50 **O34** SEQUESTRATION OF Sn2+ BY DIFFERENT LIGAND CLASSES IN AQUEOUS SOLUTION
R.M. Cigala, F. Crea, Ottavia Giuffrè, S. Sammartano
Dipartimento di Scienze Chimiche, Università di Messina

11.50-12.10 **O35** MESOPOROUS SILCIA DERIVATIZED WITH 1-(3'-AMINOPROPYL)-3-HYDROXY-2-METHYL-4-PYRIDINONE: DEVELOPMENT TRIVALENT METAL IONS SENSORS.
G. Alberti[1], R. Doi[1], R. Colleoni[1], M. Pesavento[1], M.A. Santos[2], Raffaela Biesuz[1]
[1]Dipartimento di Chimica, Università di Pavia
[2]Centro de Química Estrutural Complexo I, Instituto Superior Técnico, Lisboa (Portugal)

12.10-12.30 **O36** METHODOLOGICAL ASPECTS IN THE STUDY OF ALKALI METAL ION WEAK COMPLEXES
Silvia Berto[1], P.G. Daniele[1], G. Lando[2], E. Prenesti[1], S. Sammartano[2]
[1]Dipartimento di Chimica, Università di Torino
[2]Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università degli Studi di Messina

12.40-14.00 ***Pranzo***

14.00-15.00 **Sessione poster 2**

SALA AGAVE
PRESIEDE: **Roberto Frache**
15.00-15.40 **Premio Mazzucotelli**

SALA OLEANDRO
PRESIEDE: **Giuseppe Palleschi**
15.00-15.30 **Keynote**
KL01 GREENING UNIVERSITY
Francesco Dondi, L. Pasti, S. Riberti
Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara

Sessione Parallela 2c: Spettroscopia analitica
SALA AGAVE

PRESIEDE: **Giuseppe Spoto**
15-40-16.00 **O37** MicroRNAs DETECTION IN A DROPLET MICROFLUIDIC DEVICE
Maria Chiara Giuffrida[1], R. D'Agata[1], M.L. Zanoli[1], G. Spoto [1,2]
[1]Dipartimento di Scienze Chimiche, Università degli Studi di Catania
[2]Consorzio I.N.B.B., Roma.
16.00-16.20 **O38** SURFACE CHARACTERIZATION OF NOVEL ANTIBACTERIAL ANODIC SPARK DEPOSITION TREATMENTS FOR TITANIUM SUBSTRATES
Elvira De Giglio[1], S. Cometa[2], C. Della Valle[3], R. Chiesa[3], L. Sabbatini[1]
[1]Dipartimento di Chimica, Università degli Studi di Bari
[2]Jaber Innovation s.r.l., Roma.
[3]Dipartimento di Chimica, Materiali and Ingegneria Chimica, Politecnico di Milano
16.20-16.40 **O39** ANALYTICAL CHARACTERIZATION OF HYBRID COPPER-CHITOSAN NANOANTI-MICROBIALS SYNTHETIZED BY FEMTOSECOND LASER-ABLATION IN LIQUID
A. Ancona[1], R.A. Picca[2], A. Trapani[3], E. Bonerba[4], C. Palazzo[3], M.C. Sportelli[2], P.M. Lugarà[1,5], G. Tantillo[4], G. Trapani[3], Nicola Cioffi[2]
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[3]Dip. Farmaco Chimico, Università degli Studi di Bari
[4]Dip. di Medicina Veterinaria, Università di Bari
[5]Dip. Interateneo di Fisica, Università di Bari

16.40-17.10 ***Coffee break***

PRESIEDE: **Antonella Rossi**
17.10-17.30 **O40** USE OF 1,8-BIS(DIMETHYL-AMINO)NAPHTHALENE/9-AMINOACRIDINE AS A NEW BINARY MATRIX FOR PROFILING

OF WHOLE CELL BACTERIA BY MATRIX ASSISTED LASER DESORPTION IONIZATION MASS SPECTROMETRY.
C.D. Calvano[1], A.Monopoli[1], N. Ditaranto[1], F. Palmisano[1,2]
[1]Dipartimento di Chimica, Università degli Studi di Bari
[2]Centro Interdipartimentale di Ricerca S.M.A.R.T., Università degli Studi di Bari

17.30-17.50 **O41** MEASUREMENT OF ISOTOPIC COMPOSITION OF ATMOSPHERIC LEAD IN POLAR REGIONS BY REACTION CELL INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY
Andrea Bazzano, F. Ardini, M. Grotti
Dipartimento di Chimica e Chimica Industriale, Università di Genova

Sessione Parallela 2d: Alimenti e nutraceutici
SALA OLEANDRO

PRESIEDE: **Aldo Laganà**

15.30-15.50 **O42** DEVELOPMENT AND CHARACTERIZATION OF ACTIVE ANTIMICROBIAL PACKAGING OBTAINED BY SOL-GEL TECHNIQUE
Claudio Corradini[1,2], I. Alfieri[1,2], A. Cavazza[1,2], C. Lantano[1], A. Lorenzi[1,2], A. Montenero[1,2], N. Zucchetto[2]
[1]Dip. di Chimica, Università degli Studi di Parma
[2]Centro interdipartimentale CIPACK Università degli Studi di Parma

15.50-16.10 **O43** CHEMILUMINESCENCE-BASED BIOSENSOR FOR FUMONISINS AND AFLATOXINS QUANTITATIVE DETECTION IN MAIZE SAMPLES
Martina Zangheri[1], M. Mirasoli[1], L. Anfossi[2], D. Calabria[1], C. Passini[2], C. Baggiani[2], A. Roda[1]
[1]Department of Chemistry, University of Bologna
[2]Department of Analytical Chemistry, University of Torino

16.10-16.30 **O44** OPTIMIZATION OF THE EXTRACTION OF THE VOLATILE FRACTION FROM HONEY SAMPLES BY SPME-GC-MS, EXPERIMENTAL DESIGN AND MULTIVARIATE TARGET FUNCTIONS BASED ON PRINCIPAL COMPONENT ANALYSIS
E. Robotti, M. Bobba, Marcello Manfredi, E. Mazzucco, E. Marengo
Dipartimento di Scienze e Innovazione tecnologica, Università del Piemonte Orientale

16.30-17.00 ***Coffee break***

PRESIEDE: **Tommaso Cataldi**

17.00-17.20 **O45** TERROIR DIFFERENTIATION OF LAMBRUSCO PDO WINES BY STRONTIUM ISOTOPIC SIGNATURE
C. Baschieri[1], A. Berni[1], Lucia Bertacchini[1], M. Cocchi[1], C. Durante[1], M. Li Vigni[1], D. Manzini[2], A. Marchetti[1], S. Sighinolfi[1]
[1]Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia

[2]Centro Interdipartimentale Grandi Strumenti (CIGS), Università di Modena e Reggio Emilia

17.20-17.40 **O46** CHARACTERIZATION OF THE UNSAPONIFIABLE FRACTION OF OLIVE OIL FROM UNRIPED FRUITS AND ITS APPLICATION IN THE TREATMENT OF RHEUMATOID ARTHRITIS

Fabrizio Gelmini, V. Bianchi, R. Maffei Facino

Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano

17.40-18.00 **O47** GLUCOSINOLATES AND ACYL CONJUGATES DIVERSITY IN B. vulgaris SEEDS EVALUATED BY LC/MS USING FOURIER-TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY AND INFRARED MULTIPHOTON DISSOCIATION (FTICR-MS IRMPD)

Giuliana Bianco[1], F. Lelario[1], R. Pascale[1], S.A. Bufo[1], T.R.I. Cataldi[2]

[1]Dipartimento di Scienze, Università degli studi della Basilicata

[2]Dipartimento di Chimica, Università degli Studi di Bari

18.10-18.50 ***Presentazione dell'Area Marina Protetta di Portofino***

19.00 **Riunioni gruppi**

Mercoledì 18 Settembre 2013

Sessione Plenaria 3
SALA AGAVE

PRESIEDE: **Emanuele Magi**

9.00-9.45 **Sessione Plenaria 3**

PL03 TRACE ELEMENT SPECIATION FOR ENVIRONMENT, FOOD AND HEALTH

D. Schimek, S. Kokarnig, D. Kuehnelt, G. Raber, Kevin A. Francesconi

Institute of Chemistry-Analytical Chemistry, University of Graz, Universitaetsplatz 1, 8010 Graz, Austria.

Sessione Parallela 3a: Ambiente
SALA AGAVE

PRESIEDE: **Claudio Minero**

10.00-10.20 **O48** EMERGING POLLUTANTS IN RIVER WATER: NON-TARGET ANALYTICAL DETERMINATION OF THEIR TRANSFORMATION PRODUCTS

Paola Calza[1], C. Medana[2], M. Sarro[1], F. Dal Bello[2], C. Baiocchi[2], C. Minero[1]

[1]Dipartimento di Chimica, Università di Torino

[2]Dipartimento di Biotecnologie Molecolari e Scienze della Salute, Università di Torino

10.20-10.40 **O49** ARCTIC AEROSOL MEASUREMENTS: SAMPLING STRATEGIES AND FIRST RESULTS.

Roberto Udisti[1], S. Becagli[1], G. Calzolai[2], D. Cappelletti[3], D. Frosini[1], F. Lucarelli[2], A. Lupi[4], M. Malandrino[5], M. Mazzola[4], B. Moroni[3], S. Nava[2], M. Severi[1], R. Traversi[1], V. Vitale[4].

[1]Dept. of Chemistry, University of Florence

[2]Dept. of Physics and Astronomy, University of Florence and INFN Florence

[3]DICA and SMAArt, University of Perugia.

[4]ISAC CNR, Bologna, Italy.

[5]Dept. of Chemistry, University of Turin

10.40-11.00 **O50** INTEGRATION OF DIFFERENT MASS SPECTROMETRY TECHNIQUES TO STUDY BIOGENIC SECONDARY ORGANIC AEROSOL FORMATION

Chiara Giorio, B.M. Mahon, P.J. Gallimore, S.J. Fuller, I. Kourtchev, M. Kalberer

Department of Chemistry, University of Cambridge, UK

11.00-11.30 ***Coffee break***

PRESIEDE: **Giuseppe Scarponi**

11.30-11.50 **O51** DEVELOPMENT OF AN ANALYTICAL APPROACH FOR THE IDENTIFICATION OF FRESHWATER CYANOTOXINS BY USING A LIQUID CHROMATOGRAPHY-QTOF SYSTEM

Sara Bogialli[1], A. Pivato, C. Bortolini[1], F. Nigro Di Gregorio[2,3], L. Lucentini[2], P. Pastore[1]

[1]Department of Chemical Sciences, University of Padua

[2]Department of Environment and Primary Prevention, Italian National Institute of Health, Roma

[3]University of Rome "Sapienza", Department of Chemistry and Drug Technologies

11.50-12.10 **O52** ADVANCES IN TD/GC-MS UNTARGETED COMPOUND ANALYSIS ON PARTICULATE MATTER BEYOND PAHS ROUTINE MONITORING

Sabina Licen[1], A. Tolloi[1], G. Adami[1], S. Cozzutto[2], P. Barbieri[1,2]

[1]Dip. di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste

[2]ARCO Solutions srl, spin-off company of the Dip. di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste

12.10-12.30 **O53** UHPLC-TOF MS/MS DEGRADATION STUDIES OF TRICYCLAZOLE FUNGICIDE

Eleonora Mazzucco[1], F. Gosetti[1], U. Chiuminatto[2], R. Mastroianni[3], M.C. Gennaro[1], E. Marengo[1]

[1]Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale

[2]AB Sciex, Brugherio (MB)

[3]Merck Serono, Colleretto Giacosa (TO)

Sessione Parallela 3b: Spettrometria di massa

SALA OLEANDRO

PRESIEDE: **Maria Careri**

10.00-10.20 **O54** THE ROLE OF MASS FRACTIONATION PROCESSES IN Hg ISOTOPE RATIOS MEASUREMENTS

Carlo Baschieri[1], A. Berni[1], L. Bertacchini[1], C. Durante[1], M. Silvestri[1], A. Marchetti[1], S. Covelli[2], A. Emili[2], M.C. Rossi[3]

[1]Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia

[2]Dipartimento di Matematica e Geoscienze, Università di Trieste

[3]Centro Interdipartimentale Grandi Strumenti, Università Modena e Reggio Emilia

10.20-10.40 **O55** A NEW CLASS OF ANTIOXIDANT COMPOUNDS IN VIRGIN OLIVE OIL: N-O SUBSTITUTED PHENYLALANINE N-HYDROXY

Chiara Cavaliere, V. Colapicchioni, R. Samperi, S. Stampachiacchiere, A. Laganà

Dipartimento di Chimica, Sapienza Università di Roma

10.40-11.00 **O56** ULTRA-HIGH PRESSURE LIQUID CHROMATOGRAPHY-TANDEM HIGH RESOLUTION MASS SPECTROMETRY FOR TARGETED AND UNTARGETED ANALYSIS OF POTENTIAL MIGRANTS FROM POLYCARBONATE FOOD-CONTACT PLASTICS

Chiara Bignardi, A. Cavazza, C. Corradini, P. Salvadeo

Dipartimento di Chimica, Università degli Studi di Parma

11.00-11.30 ***Coffee break***

PRESIEDE: **Achille Cappiello**

11.30-11.50 **O57** A VISCOUS FILM SAMPLE CHAMBER FOR LASER ABLATION INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY
Damiano Monticelli, D. Civati, S. Recchia
Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria

11.50-12.10 **O58** NON-TARGET UHPLC-HIGH RESOLUTION TANDEM MASS SPECTROMETRY ANALYSIS OF PHOTOIRRADIATED RED BEVERAGES
Fabio Gosetti[1], U. Chiuminatto[2], E. Mazzucco[1], R. Mastroianni[3], M.C. Gennaro[1], E. Marengo[1]
[1]Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale
[2]AB Sciex, Brugherio (MB)
[3]Merck Serono, Colleretto Giacosa (TO)

12.10-12.30 **O59** MALDI IMAGING OF NEUROTRANSMITTER TRANSPORTER-LINKED SIGNALING NETWORKS
Rosalia Zianni[1,2], Y. Ran[3], J. Norris[1], R. Blakely[3], T.R.I Cataldi[2], R.M. Caprioli[1]
[1]Mass Spectrometry Research Center and Department of Biochemistry, Vanderbilt University School of Medicine, Nashville, USA.
[2]Dipartimento di Chimica, Università degli Studi di Bari
[3]Department of Pharmacology, Vanderbilt University School of Medicine, Nashville, USA.

12.40-14.00 ***Pranzo***

14.30-15.30 **Sessione poster 3**

Sessione Parallela 3c: Ambiente e green chemistry

SALA AGAVE

PRESIEDE: **Carlo Barbante**

15-30-15.50 **O60** GREEN PHOTOCATALYTIC HYDROGEN PRODUCTION FROM OLIVE MILL WASTEWATER
Andrea Speltini, M. Sturini, F. Maraschi, D. Dondi, G. Fisogni, A. Profumo, A. Albini, A. Buttafava
Dipartimento di Chimica, Università di Pavia

15.50-16.10 **O61** LABORATORY SIMULATION OF A GLUCOSE-INDUCED REDOX TREATMENT FOR IN-SITU REMEDIATION OF GROUNDWATER POLLUTED BY HEXAVALENT CHROMIUM
Marco Ginepro[1], V.Zelano[1], A. Bianco Prevot[1], J. Tafur[1], D. De Luca[2]
[1]Dipartimento di Chimica, Università di Torino
[2]Dipartimento di Scienze della Terra, Università di Torino

16.10-16.30 **O62** RICE HUSK AS BIOSORBENT FOR WASTEWATER REMEDIATION AND SPE PRECONCENTRATION OF FLUOROQUINOLONE ANTIBIOTICS

Elisa Rivagli, F. Maraschi, M. Sturini, A. Speltini, A. Profumo
Dipartimento di Chimica, Università degli Studi di Pavia

16.30-17.00 ***Coffee break***

PRESIEDE: **Roger Fuoco**

17.00-17.20 **O63** METAL STRATIGRAPHIES FROM ANTARCTIC MARINE SEDIMENTS: HINTS FOR PALEOCLIMATIC RECONSTRUCTIONS
Rita Traversi[1], S. Becagli[1], E. Colizza[2], D. Frosini[1], G. Gori[1], M. Marconi[1], R. Melis[2], K. Mezgec[3], M. Severi[1], B. Stenni[2], R. Udisti[1]
[1]Dept. of Chemistry, Univ. of Florence
[2]Dept. of Mathematics and Geosciences, Univ. of Trieste
[3]Dept. of Environment, Earth and Physical Science, Univ. of Siena

17.20-17.40 **O64** DETERMINATION OF POPs FROM COMBUSTION OF VINEYARD PRUNING RESIDUES IN CONTROLLED SYSTEM
E. Marchiori[1], C. Giorio[2], A. Perazzolo[3], S. Zambon[1], L. Soldà[3], Andrea Tapparo[3], R. Piazza[1,4]
[1]Department of Environmental Sciences, Informatics and Statistics, Ca'Foscari University, Venice
[2]Department of Chemistry, University of Cambridge, UK.
[3]Department of Chemical Sciences, University of Padova
[4]CNR-IDPA, Venice

17.40-18.00 **O65** ANALYSIS OF ORGANIC SPECIES IN AIRBORNE PARTICULATE MATTERT
Paola Fermo[1], C.A. Belis[2], F. Gelmini[3], R. Gonzalez[1], R. Maffei Facino[1,2], A. Piazzalunga[1], J. Cancelinha[2], V. Pedroni[2], R. Vecchi[4]
[1]Dipartimento di Chimica, Università di Milano
[2]JRC-European Commission, Ispra (VA)
[3]Dipartimento di Scienze Farmaceutiche, Università di Milano
[4]Dipartimento di Fisica, Università di Milano

Sessione Parallela 3da: Spettrometria di massa
SALA OLEANDRO

PRESIEDE: **Innocenzo G. Casella**

15-30-15.50 **O66** FEASIBILITY OF DIRECT-EI LC-MS AS A TOOL FOR FOOD SAFETY APPLICATIONS: IDENTIFICATION AND QUANTITATION OF ENVIRONMENTAL CONTAMINANTS IN MILK POWDER.
A. Cappiello[1], G. Famiglini[1], Veronica Termopoli[1], P. Palma[1], F. Capriotti[1], N. Cellar[2]
[1]DiSTeVA, Università degli Studi di Urbino
[2]Abbott Nutrition, Columbus, Ohio, USA

15.50-16.10 **O67** COMPREHENSIVE STUDY OF PCBs BEHAVIOUR IN AN ION TRAP MASS SPECTROMETER AND OPTIMIZATION OF INSTRUMENTAL PARAMETERS FOR TANDEM MASS ANALYSIS
Riccardo Narizzano[1], Fulvia Risso[1], A. Magherini[1], G. Cordone[1,2], S. Maggiolo[1], M. Di Carro[2], E. Magi[2]

[1]Regional Agency for Environmental Protection–Liguria (ARPAL), Genoa
[2]Department of Chemistry and Industrial Chemistry, University of Genoa

16.10-16.30 **O68** THERMAL DEGRADATION STUDIES OF ULTRA-THIN POLYMER FILMS BY ONLINE TGA-GC-MS ANALYSIS.
Valentina Gianotti[1], D. Antonioli[1], K. Sparnacci[1], M. Laus[1], M. Perego[2], F. Ferrarese Lupi[2], T. J. Giammaria[1,2], G. Seguini[2]
[1]DiSIT, Università del Piemonte Orientale
[2]Laboratorio MDM, IMM-CNR, Agrate Brianza

16.30-17.00 ***Coffee break***

Sessione Parallela 3db: Sensori
SALA OLEANDRO

PRESIEDE: **Cosimino Malitesta**

17.00-17.20 **O69** AMPEROMETRIC MINIPLATFORM FOR ISOPROPYL-9H-THIOXANTHONE DETECTION BASED ON MOLECULARLY IMPRINTED POLYMER
Girolamo D'Agostino, G. Alberti, R. Biesuz, M. Pesavento
Department of Chemistry, University of Pavia

17.20-17.40 **O70** ALLOSTERICALLY-TUNABLE, DNA-BASED SWITCHES TRIGGERED BY HEAVY METAL
Alessandro Porchetta[1,2], G. Palleschi[1], F. Ricci[1,2]
[1]Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma
[2]Consorzio Interuniversitario Biostrutture e Biosistemi "INBB", Roma

17.40-18.00 **O71** AGENT ORANGE HERBICIDES, ORGANOPHOSPHATE AND TRIAZINIC PESTICIDES ANALYSIS USING NEW ORGANIC PHASE IMMUNOSENSORS
E. Martini, Mauro Tomassetti, G. Merola, L. Campanella
Department of Chemistry, University of Rome "Sapienza"

18:15 **Assemblee gruppi**

20.30 ***Cena di Gala***

Giovedì 19 Settembre 2013

Sessione Plenaria 4
SALA AGAVE

PRESIEDE: **Renato Seeber**

9.00-9.45 **Sessione Plenaria 4**

PL04 SIMPLE AND EFFICIENT NANOBIOSENSING DEVICES USING PLASTIC AND PAPER BASED PLATFORMS

Arben Merkoçi

ICREA & Nanobioelectronics & Biosensors Group,Catalan Institute of Nanoscience and Nanotechnology (ICN2), Campus de la UAB, 08193 Bellaterra (Barcelona), Spain

Sessione Parallela 4a: Sensori ed elettroanalisi
SALA AGAVE

PRESIEDE: **Paolo Ugo**

10.00-10.20 **O72** PYROLIZED PHOTORESIST CARBON ELECTRODES: APPLICATION TO HEAVY METAL ANALYSIS

Andrea Mardegan[1,2], M. Cettolin[1], R. Kamath[3], P. Scopece[2], M. Madou[3,4] and P. Ugo[1]

[1]Department of Molecular Sciences and Nanosystems, University Ca' Foscari of Venice

[2]Veneto Nanotech, Venice-Marghera

[3]Department of Biomedical Engineering, University of California, USA

[4]Department of Mechanical and Aerospace Engineering, University of California, USA

10.20-10.40 **O73** PROTECTIVE COATINGS INFLUENCE ON OXYGEN OPTICAL SENSORS SIGNAL

Andrea Mondin, D. Badocco, P. Pastore

Dipartimento di Scienze Chimiche, Università di Padova

10.40-11.00 **O74** ELECTROANALYTICAL APPLICATIONS OF A CARBON-Au NANOPARTICLES COMPOSITE INCLUDED IN A SOLGEL MATRIX

Chiara Zanardi[1], J.R. Crespo-Rosa[2], M. ElKaoutit[2], F. Terzi[1], L. Pigani[1], R. Seeber[1], I. Naranjo-Rodriguez[2]

[1]Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia

[2]Department of Analytical Chemistry, University of Cadiz, Spain

11.00-11.30 ***Coffee break***

PRESIEDE: **Paolo Pastore**

11.30-11.50 **O75** GOLD NANO-PARTICLES-PEPTIDE BASED GAS SENSORS ARRAY: COMPUTATIONAL STUDY AND PRACTICAL APPLICATIONS

Daniel Pizzoni[1], M. Mascini[1], M. Del Carlo[1], V. Lanzone[1], C. Di Natale[2], D. Compagnone[1]

[1]Facoltà di Bioscienze e Tecnologie Agro-Alimentari e Ambientali, Università degli studi di Teramo

[2]Dipartimento di Ingegneria Elettronica, Università di Tor Vergata

11.50-12.10 **O76** SCREEN-PRINTED ELECTRODES MODIFIED WITH NANOSTRUCTURED CARBON BLACK AS PLATFORM TO DEVELOP SENSORS AND BIOSENSORS
Fabiana Arduini[1], A. Amine[2], M. Forchielli[1], D. Neagu[1], S. Cinti[1], G. Vellucci[1], I. Cacciotti[3], F. Nanni[3], G. Palleschi[1], D. Moscone[1]
[1]Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata
[2]Faculté de Sciences et Techniques de Mohammadia, Morocco
[3]Dipartimento di Ingegneria Industriale, Università di Roma Tor Vergata, Roma.

12.10-12.30 **O77** COMPOSITE ELECTRODES BASED ON NANOTUBES-/POLYDISPERSED METAL PARTICLES. A VOLTAMMETRIC AND MORPHOLOGICAL STUDY.
Innocenzo Giuseppe Casella, M. Contursi.
Dipartimento di Scienze. Università degli Studi della Basilicata

Sessione Parallela 4b: Chimica Analitica Forense,Tossicologia, Salute Umana
SALA GINEPRO

PRESIEDE: **Marco Vincenti**

10.00-10.20 **O78** CAVITAND-BASED MATERIALS FOR THE DETERMINATION OF NITROAROMATIC EXPLOSIVES AND EXPLOSIVE TAGGANTS
Federica Bianchi[1], A. Bedini[1], A. Gregori[2], E. Dalcanale[1], M. Careri[1]
[1]Dipartimento di Chimica, Università degli Studi di Parma
[2]Raggruppamento Carabinieri Investigazioni Scientifiche di Parma, Parma

10.20-10.40 **O79** EXTRACTION STRATEGIES FOR THE DETERMINATION OF DRUGS OF ABUSE IN BIOLOGICAL MATRICES
Manuel Sergi[1], C. Montesano[2], M. Mascini[1], D. Compagnone[1], R. Curini[2]
[1]Facoltà di Bioscienze e Tecnologie Agro-alimentari e Ambientali, Università degli Studi di Teramo
[2]Dipartimento di Chimica, Sapienza Università di Roma

10.40-11.00 **O80** CHEMOMETRIC APPROACH TO OPEN VALIDATION PROTOCOLS. PREDICTION OF VALIDATION PARAMETERS IN UHPLC-MS/MS METHODS FOR LARGE SETS OF ANALYTES
Eugenio Alladio[1], A. Salomone[2], V. Pirro[1,2], D. Di Corcia[2], M. Vincenti[1,2]
[1]Dipartimento di Chimica, Università degli Studi di Torino
[2]Centro Regionale Antidoping, Orbassano (TO)

11.00-11.30 ***Coffee break***

PRESIEDE: **Giuseppe Palleschi**

11.30-11.50 **O81** PLASTIBODIES INSTEAD OF ANTIBODIES? TOWARDS WORKING ENZYME-BASED MOLECULARLY IMPRINTED SORBENT ASSAYS (E-MISAs)

Cinzia Passini[1], L. Anfossi[1], A. Bossi[2], C. Giovannoli[1], C. Baggiani[1]
[1]Dipartimento di Chimica, Università di Torino
[2]Dipartimento di Biotecnologie, Università di Verona

11.50-12.10 **O82** BIOLUMINESCENCE HELPS MALARIA RESEARCH: EXPLOITING NEW LUCIFERASES TO IMPROVE ANALYTICAL PERFORMANCE OF ANTIMALARIAL SCREENING ASSAYS.
Luca Cevenini[1], G. Camarda[2], E. Michelini[1], M. M. Calabretta[1], G. Siciliano[2], B.R. Branchini[3], P. Alano[2], A. Roda[1]
[1]Department of Chemistry, University of Bologna
[2]Department of Infectious, Parasitic and Immunomediated Diseases, Istituto Superiore di Sanità, Rome
[3]Department of Chemistry, Connecticut College, New London, Connecticut, USA

12.10-12.30 **O83** SOLUTIONS FOR FORENSIC TOXICOLOGY USING LC-HRMS WITH INTUITIVE DATA PROCESSING TOOLS.
Stefano Fiorina[1], A. Taylor[2]
[1]AB SCIEX Srl, Brugherio, MB, Italy
[2]AB SCIEX Inc, Concord, ON, Canada

SALA AGAVE

12.30–12.45 **Chiusura del Congresso**

13.00-14.30 ***Pranzo***

Sessione Poster I (Lunedì 16 Settembre 14.30-15.30)

P01 ELECTROCHEMICAL IMMUNOSENSOR FOR HEPATITIS A DETERMINATION.
C. Travali[1], L. Micheli[1], A. De Stefano[1], D. Donia[2], M. Divizia[2], G. Palleschi[1]
[1]Dip. di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata
[2]Dip. di Medicina sperimentale e Chirurgia, Università di Roma Tor Vergata

P02 CHROMATOGRAPHIC CHARACTERIZATION OF PROPOLIS SPECIMENS FROM CALIFORNIA AND OREGON.
A. Aliboni
Dip. UTRINN-BIO, ENEA CRE Casaccia, Santa Maria di Galeria (RM)

P03 RAPID DETECTION OF VIABLE AND NON-VIABLE PATHOGEN BACTERIA BY A MOS-ARRAY OLFACTORY SENSOR COMBINED WITH FIELD-FLOW FRACTIONATION TECHNOLOGY.
B. Roda[1], C. Colliva[1], M. Mirasoli[1], P. Reschiglian[1], S. Lanteri[2], A. Roda[1]
[1]Department of Chemistry, University of Bologna
[2]Department of Pharmacy, University of Genoa

P04 PEPTIDE PROFILING IN CHEESE SAMPLES BY LC-TANDEM MASS SPECTROMETRY.
D. Nardiello, A. Natale, C. Palermo, A. Conte, A. Lucera, M.A. Del Nobile, D. Centonze
Dipartimento di Scienze Agrarie, degli Alimenti e dell'Ambiente, Università degli Studi di Foggia

P05 ANALYTICAL STRATEGIES FOR THE NON INVASIVE ANALYSIS OF LACTATE IN SPORT AND CLINICS.
D. Pellegrini[1], M. Onor[1], M.P. Colombini[2] and E. Bramanti[1]
[1]C.N.R., Institute of Chemistry of Organometallic Compounds, Pisa.
[2]Dept. of Chemistry and Industrial Chemistry, University of Pisa

P06 SCREENING OF CYANOBACTERIAL HEPATOTOXINS IN WATER SAMPLES: OPTIMIZATION OF A COLORIMETRIC PHOSPHATASE INHIBITION METHOD.
K. Petropoulos, L. Micheli, G. Volpe, D. Moscone, G. Palleschi
Dip. di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata

P07 IMPROVEMENTS IN THE DETERMINATION OF SULFIDE, CYANIDE AND THIOCYANATE BY CHEMICAL VAPOR GENERATION COUPLED WITH HS-GC-MS.
M. Onor[1], S. Ammazzini[1,2], E. Pagliano[3], E. Pitzalis[1], E. Bramanti[1] and A. D'Ulivo[1]
[1]C.N.R., Institute of Chemistry of Organometallic Compounds, Pisa
[2]University of Pisa, Department of Chemistry and Industrial Chemistry
[3]National Research Council Canada, Ottawa, Canada

P08 A NEW GALACTURONIC ACID BIOSENSOR BASED ON A RECOMBINANT URONATE DEHYDROGENASE ENZYME FROM *PSEUDOMONAS SYRINGAE.*
R. Antiochia[1], H. Boer[2], G. Favero[1], F. Mazzei[1], C. Tortolini[1]
[1]Dip. di Chimica e Tecnologie del Farmaco, Sapienza Università di Roma
[2]VTT Technical Research Centre of Finland, Finland

P09 DETERMINATION OF ANTICOAGULANT DRUGS AND THEIR METABOLITES IN ORAL FLUID: STRATEGIES FOR SAMPLE COLLECTION.
R. Fuoco[1], T. Lomonaco[1], S. Ghimenti[1], I. Piga[1], D. Biagini[1], M. Onor[2], A. Paolicchi[3], L. Ruocco[4], G. Pellegrini[4], M. G. Trivella[5], F. Di Francesco[1,5].
[1]Department of Chemistry and Industrial Chemistry, University of Pisa
[2]Institute of Chemistry of Organometallic Compounds, CNR, Pisa

[3]Department of Translational Research and New Technologies in Medicine and Surgery, University of Pisa
[4]Chemical-Clinical Analysis Laboratory, AOUP, Pisa
[5]Institute of Clinical Physiology, CNR, Pisa

P10 DIFFERENTIAL PROTEOMIC ANALYSIS OF PRIMING-INDUCED SALT TOLERANCE IN DURUM WHEAT.

S. Stampachiacchiere, L. Bacci, A.L. Capriotti, P. Foglia, E. Lisi, R. Samperi, A. Laganà

Dipartimento di Chimica, Sapienza Università di Roma

P11 EQUILIBRIUM BINDING LANGMUIR ISOTHERMS FOR DIFFERENT BILE ACIDS TO CHOLESTYRAMINE AND COLESEVELAM RESINS.

S. Spinozzi[1], C. Camborata[1], C.a Colliva[1], A. F. Hofmann[2] A. Roda[1]

[1]Department of Chemistry, University of Bologna
[2]Division of Gastroenterology, University of San Diego, USA

P12 SHOTGUN PROTEOMICS CHARACTERIZATION OF SERUM PROTEINS ADSORBED ONTO PEG-MODIFIED LIPOSOME NANOPARTICLES.

S. Piovesana[1], G. Caracciolo[2], C. Cavaliere[1], P. Foglia[1], D. Pozzi[2], R. Samperi[1], A. Laganà[1]

[1]Dipartimento di Chimica, Sapienza Università di Roma
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P13 THE TIME EVOLUTION OF NANOPARTICLE-PROTEIN CORONA IN HUMAN PLASMA: A PROTEOMIC APPROACH.

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P14 COMPUTATIONAL DESIGN AND SELECTION OF BIOMIMETIC RECEPTORS FOR PESTICIDES SELECTIVE EXTRACTION.

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P15 TOWARDS THE INTEGRATION OF REAL TIME PCR IN LAB ON CHIP DEVICES.

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P16 ON-CHIP CHEMILUMINESCENCE DETECTION OF ENZYME LABELS BY MEANS OF INTEGRATED AMORPHOUS SILICON PHOTODIODES.

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P17 EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE ACTION OF CHLOROSULPHONATED PARAFFINS ON COLLAGEN MATRICES.

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P18 PROTON COUPLED ELECTRON TRANSFER IN ADENOSINE SELF-AGGREGATES.

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P19 STACKING INTERACTIONS BETWEEN ADENINES IN DNA OLIGONUCLEOTIDES.

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P20 DNA LABELLED NANOPARTICLES FOR IMPROVED SURFACE PLASMON RESONANCE IMAGING.

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P21 DETERMINATION OF SHIKIMIC, JASMONIC AND SALYCILIC ACIDS IN WILD AND OGM NICOTIANA LANGSDORFII PLANTS EXPOSED TO CHEMICAL AND WATER STRESSES.

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P22 MEASUREMENTS OF VOLATILE ORGANIC COMPOUNDS IN INDOOR AIR OF FLORENTINE MUSEUMS

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P23 THE ROLE OF ENVIRONMENTAL POLLUTANTS ON THE DEGRADATION OF PAINT VARNISHES IN MUSEUM AND MICROCLIMATE FRAMES.

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P24 MULTIVARIATE DATA ANALYSIS APPLIED TO THE STUDY OF CORROSION.

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P25 NEW METHODOLOGIES FOR CLEANING TREATMENT OF PAPER ARTWORKS: SOME CASE STUDIES.

L. Micheli[1] C. Mazzuca[1], E. Cervelli[1], A. Palleschi[1], G. Palleschi[1], R. Montalto[1] , C. Crestini[1], S. Iannuccelli[2], S. Sotgiu[2].
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P26 NON-DESCTRUCTIVE IDENTIFICATION OF CONSERVATION TREATMENTS OF THE DEAD SEA SCROLLS BY USING DART-MS.

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P27 STATISTICAL ANALYSIS OF AMINO ACID FINGERPRINT TO CHARACTERIZE PROTEIN BINDERS IN WORKS OF ART.

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P28 INTEGRATED MASS SPECTROMETRY APPROACH FOR THE CHEMICAL CHARACTERIZATION OF ORIGINAL PAINT TUBES USED BY EDVARD MUNCH.

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P29 LIQUID CHROMATOGRAPHY-HIGH RESOLUTION MASS SPECTROMETRY-BASED METHOD TOWARDS THE COMPREHENSIVE ANALYSIS OF MIGRATION OF PRIMARY AROMATIC AMINES FROM FOOD PACKAGING.

M. Mattarozzi[1,2], F. Lambertini[3], M. Giannetto[1,2], M. Suman[3], F. Bianchi[1], M. Careri[1,2]
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P30 CALIBRATION AND PERFORMANCE EVALUATION OF A PULSED REPETITIVE INTERFACE FOR ONLINE TGA-GC-MS ANALYSIS; APPLICATION TO THE CHARACTERISATION OF COMPLEX LDH SAMPLES.

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P31 APPROACHES TO IMPRINTED THIN LAYERS FOR CAPILLARY ELECTROCHROMATOGRAPHY.

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P32 VARIATIONS OF THE CONTENT OF PHENOLIC ACIDS IN DURUM WHEAT AS A FUNCTION OF GENOTYPE AND ENVIRONMENT.

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P33 HIGH THROUGHPUT ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY TRACE ANALYSIS OF PERFLUORINATED COMPOUNDS IN MILK.

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P34 FUNCTIONALIZATION OF MESOPOROUS SILICA BY A CAGE-TYPE ANION RECEPTOR (L-MS): BEHIND THE DEVELOPMENT OF A CHLORIDE SENSOR.

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P35 CORE SHELL STATIONARY PHASES FOR A NOVEL SEPARATION OF TRIGLYCERIDES IN PLANT OILS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH ELECTROSPRAY-QUADRUPOLE-TIME OF FLIGHT MASS SPECTROMETER.

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Sessione Poster II (Martedì 17 Settembre 14.00-15.00)

P36 QUALITY BY DESIGN AND CAPILLARY ELECTROPHORESIS FOR DEVELOPING ORALLY DISINTEGRATING TABLETS CONTAINING FROVATRIPTAN.
N. Mennini, S. Furlanetto, S. Orlandini, B. Pasquini, P. Mura
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P37 EXPERIMENTAL DESIGN METHODOLOGIES IN THE DEVELOPMENT OF MUCOADHESIVE WAFERS LOADED WITH ECONAZOLE.
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P38 DATA FUSION PROTOCOLS FOR FOOD AUTHENTICATION.
Biancolillo A., Bevilacqua M., Bucci R., Magrì A.L., Magrì A.D., Marini F.
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P39 AN INTEGRATED QUALITY BY DESIGN APPROACH TOWARDS THE DESIGN SPACE DEFINITION OF A CAPILLARY ELECTROPHORESIS METHOD FOR THE ANALYSIS OF TRIPTANS.
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P40 NEAR INFRARED SPECTROSCOPY FOR NON-DESTRUCTIVE CHARACTERIZATION OF TOMATO CULTIVAR. A PILOT STUDY ON 'CUORE DI BUE DI ALBENGA'.
L. Bagnasco[1], M.C. Casolino[1], L. Medini[2], P. Oliveri[1], R. Simonetti[1], S. Lanteri[1]
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P41 EVALUATION OF THE EFFECT OF RED CHILLI ADDITION TO FOOD PRODUCTS ON THEIR SHELF-LIFE.
C. Bignardi[1], A. Cavazza[1], C. Corradini[1], S. Corno[2] , S. Corti[2], C. Lantano[1], G. Passoni[2]
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P42 CARBOHYDRATE-BASED BRINE COMPOSITION IN HIGH QUALITY COOKED HAM PRODUCTION.
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P43 CHARACTERIZATION OF UNIFLORAL AND MULTIFLORAL HONEYS FROM MARCHE, CENTRAL ITALY, WITH A CHEMOMETRIC APPROACH ON THE BASIS OF PHYSICOCHEMICAL ANALYSIS.
C. Truzzi[1], S. Illuminati[1], A. Annibaldi[1], C. Finale[1], M. Rossetti[2], G. Scarponi[1]
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P44 DETERMINATION AND DISTRIBUTION OF YLOID IN SOIL AND OVERALL GRAPEVINE SYSTEM (*VITIS VINIFERA* L.) BY ICP-MS TECHNIQUE. A CASE STUDY.
L. Tutone, A. Pisciotta, F. Saiano
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P45 ENHANCING CONSUMER QUALITY PERCEPTION TOWARDS PROTECTED DESIGNATION OF ORIGIN PRODUCTS BY GEOGRAPHICAL TRACEABILITY: THE CASE OF BOLOGNA POTATOES PDO.

F. Albertini[1], L. Bertacchini[2], C. Durante[2], M. Esposito[1], A. Galli[3], A. Marchetti[2], S. Paradisi[3], M. Silvestri[2] and L. Tassi[2]
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P46 RAPID DETERMINATION OF XANTHINE METABOLITES IN FOOD BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL AND UV DETECTION.

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P47 DETERMINATION OF MELAMINE IN FOOD BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY – UV DETECTOR.

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P48 VALIDATION OF A SCREENING METHOD FOR THE DETERMINATION OF NDL-PCBS IN MUSSEL SAMPLES BY GC/ECD ACCORDING TO THE RECENT REGULATION (EU) N°1259/2011.

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P49 AQUEOUS EXTRACTION AT ROOM TEMPERATURE OF STEVIOSIDES CONTENT IN DRIED LEAVES OF STEVIA REBAUDIANA BERTONI USING THE EXTRACTOR NAVIGLIO. COMPARISON WITH CONVENTIONAL HOT INFUSION.

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P50 INVESTIGATION OF DIFFERENT SAMPLE TREATMENT METHODS FOR THE LIQUID CHROMATOGRAPHY-ELECTROSPRAY-TANDEM MASS SPECTROMETRY DETECTION OF ALLERGENIC FINING AGENT RESIDUES IN RED WINE.

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P51 USE OF ROOM TEMPERATURE IONIC LIQUIDS (RTILs) FOR ELECTROCHEMICAL MEASUREMENT OF FREE ACIDITY IN OLIVE OIL

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P52 STUDY OF PROTONATION EQUILIBRIA OF SCHIFF BASE DERIVED FROM O–VANILLIN AND 1,2–DIAMINOBENZENE.

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P53 INTERACTION BETWEEN IRON(III) CATION AND SCHIFF BASE DERIVED BY O–VANILLIN AND 1,2–DIAMINOBENZENE.

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P54 THE BEHAVIOR OF ARGININE AS LIGAND TOWARD IRON (II) AND IRON (III).

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P55 A CATIONIC PORPHYRIN IN A MICELLAR MEDIUM: PRELIMINARY ANALYSIS OF SYSTEM CHARACTERISTICS AND METAL EXTRACTION ABILITY

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P56 SPECTRAL MODIFICATIONS OF SUBTERRANEAN WATERS UNDER IRRADIATION.

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P57 ANALYTICAL TESTS FOR THE CHARACTERIZATION AND VALIDATION OF MERCURY-SORBENT MATRICES.

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P58 X-RAY PHOTOELECTRON SPECTROSCOPY CHARACTERIAZATION OF AEROSOL PARTICLES IN ANTARCTICA.

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P59 ULTRA PERFORMACE LIQUID CHROMATOGRAPHY WITH FLUORESCENCE DETECTION FOR SIMULTANEOUS DETERMINATION OF ASYMMETRIC DIMETHYLARGININE, MONOMETHYLARGININE, SYMMETRIC DIMETHYLARGININE AND L-ARGININE IN BIOLOGICAL FLUIDS.

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P60 ANALYSIS OF THE ZnLMM AUGER SIGNAL OF ZnO NANOMATERIALS SYNTHESIZED BY DIFFERENT METHODS.

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P61 A MULTI-ANALYTICAL APPROACH FOR THE STUDY OF HYDROPHOBIZING COATING FOR CULTURALE HERITAGE.

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P62 CHARACTERIZATION OF AERONAUTICAL AND AEROSPACE METAL MATERIALS THROUGH THE COMPARISON BETWEEN THE XRF vs. ICP-OES AND FESEM-EDS TECHNIQUES.

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P63 SPECTROSCOPIC INVESTIGATION ON CONDUCTING POLY(O-AMINOPHENOL) ELECTROSYNTHESIZED ON PLATINUM- ELECTRODES IN ACIDIC MEDIA.

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P64 MICROFLUIDIC DEVICE: DEVELOPMENT AND TESTING OF NANOSTRUCTURED OXIDIC MATERIALS.

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P65 DETERMINATION OF CAFFEINE @ GOLD NANOPARTICLES MODIFIED GOLD (AU) ELECTRODE: A PRELIMINARY STUDY.

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P66 INFLUENCE OF DIFFERENT BIOLOGICAL ENVIRONMENTS ON THE STABILITY OF SEROTONIN DETECTION ON GOLD NANOPARTICLES MODIFIED SCREEN PRINTED ELECTRODES.

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P67 BIOMIMETIC SORBENTS AS SPE STATIONARY PHASE FOR THE DETERMINATION OF CANNABINOIDS BY LC-MS/MS.

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P68 THE INTERNATIONAL POLY IMPLANT PROTHÈSE (PIP) IMPLANTS SCANDAL: ANALYTICAL INVESTIGATIONS.

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P69 DYES AND REACH REGULATION: AN ANALYTICAL APPROACH.

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P70 CHARACTERIZATION OF NANOSILVER TEXTILES AND EVALUATION OF AG RELEASE AND PERCUTANEOUS ABSORPTION: AN IN VITRO STUDY.

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P71 PRESSURIZED LIQUID EXTRACTION FOR THE EXTRACTION OF CANNABINOIDS AND METABOLITES FROM HAIR: DETECTION OF CUT-OFF VALUES BY LC-MS/MS.

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P72 NIR SPECTROSCOPY AND CHEMOMETRICS IN FORENSIC CHEMISTRY: AKB48 DETERMINATION.

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Sessione Poster III (Mercoledì 18 Settembre 14.30-15.30)

P73 A CONGENER APPROACH TO TOTAL POLYCHLOROBIPHENYLS DETERMINATION.
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P74 SEVERAL KINDS OF SKIN INFLUENCE IN VITRO METAL NANOPARTICLES PERMEATION.
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P75 CHEMICAL FRACTIONATION OF Cd, Pb AND Cu IN ANTARCTIC AEROSOL BY SEQUENTIAL EXTRACTION (WATER-SOLUBLE, ACID EXTRACTABLE AND INERT FRACTIONS) AND SWASV DETERMINATION.
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P76 POLYBROMINATED DIPHENIL ETHERS (PBDES) DETECTION USING GC-MS, ELISA AND AN ELECTROCHEMICAL MULTIPLEXED BIOSENSOR.
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P77 PCB-11 IN ANTARCTIC LAKES AND SNOW.
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P78 POLYCYCLIC AROMATIC HYDROCARBONS IN ORANGE LEAVES IN SEVILLE (SPAIN): AN INDICATOR OF URBAN AIR CONTAMINATION LEVEL.
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P79 METALS IN ATMOSPHERIC AEROSOL FROM URBAN AND MARINE SITES IN ITALY: A COMPARISON BETWEEN PIXE AND ICP-AES MEASUREMENTS.
R. Traversi[1], S. Becagli[1], G. Calzolai[2], M. Chiari[2], D. Frosini[1], M. Giannoni[2], F. Lucarelli[2], M. Marconi[1], S. Nava[2], M. Severi[1], R. Udisti[1].
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P80 HUMIC SUBSTANCES DISTRIBUTION IN ANTARCTIC COASTAL MARINE SEDIMENTS (ROSS SEA ANTARCTICA).
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P81 EVALUATION OF TOXIC METALS BIOACCESSIBILITY IN URBAN SOILS.

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P82 APEX (AQUEOUS PHOTOCHEMISTRY OF ENVIRONMENTALLY-OCCURRING XENOBIOTICS): A NOVEL SOFTWARE TOOL TO PREDICT THE PHOTODEGRADATION OF ORGANIC POLLUTANTS IN SURFACE WATERS.

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P83 MAJOR AND TRACE ELEMENTS AND REEs CONCENTRATION IN AEROSOL SAMPLES COLLECTED AT NY-ALESUND (SVALBARD ISLANDS) DURING THE 2010 CAMPAIGN.

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P84 SOURCE APPORTIONMENT OF AEROSOL PARTICLES AT THE ARCTIC SITE OF NY ALESUND (SVALBARD ISLANDS) BY PMF ANALYSIS.

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P85 ANALYTICAL ROUTE FOR HYDROGEOLOGICAL ANOMALIES: THE CASE OF A "WHITE" SPRING IN MINE VALLEY (LIVIGNO – ITALY).

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P86 pH-STAT LEACHING TEST AUTOMATIC APPARATUS DEVELOPMENT TO CHARACTERIZE GRANULAR WASTE.

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P87 MONITORING OF H_2S REMOVAL BY GREEN SULFUR BACTERIA IN A BIOREACTOR USING GC-FPD.

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P88 DETERMINATION OF Os(VIII), Ru(III) AND Pb(II) IN VEGETABLE MATRICES, POTENTIAL BIO_MONITORS, BY SQUARE WAVE CATALYTIC ADSORPTIVE VOLTAMMETRY (SWCAdV)

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P89 CHARACTERIZATION OF THE ELEMENT CONTENT IN LACUSTRINE ECOSYSTEMS IN TERRA NOVA BAY, ANTARCTICA

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P90 DETERMINATION OF EMERGING POLLUTANTS AND ENDOCRINE DISRUPTERS IN DRINKING WATER BY LIQUID CHROMATOGRAPHY - TANDEM MASS SPECTROMETRY.

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P91 QUANTITATIVE RELATIONSHIP BETWEEN CHARGE STATE OF SODIUM DOCUSATE (AOTNA) CLUSTERS AND CONE VOLTAGE.

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P92 TANDEM MASS SPECTROMETRY WITH DATA DEPENDENT ACQUISITION FOR THE DETERMINATION OF UV FILTERS IN URBAN WASTEWATER TREATMENT PLANTS.

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P93 ULTRATHIN Si NANOWIRES AS PROMISING SUBSTRATES FOR SURFACE-ASSISTED LASER DESORPTION IONIZATION MASS SPECTROMETRY.

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P94 A STRATEGY FOR THE INTEGRATION OF RECOGNITION ELEMENTS IN EGOFET BASED BIOCHEMICAL SENSORS.

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P95 ANALYTICAL PERSPECTIVES OF TAURINE/GRAPHITE OXIDE ELECTRODE COATINGS.

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P96 COMPARING REGRESSION RELATIONSHIPS: APPLICATION TO CHEMICALLY MODIFIED ELECTRODES.

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P97 MICROSTRUCTURING CONDUCTING POLYMERS AND MOLECULARLY IMPRINTED POLYMERS BY LIGHT-ACTIVATED ELECTROPOLYMERIZATION ON MICROMACHINED.
SILICON. APPLICATIONS IN ELECTROCHEMICAL SENSING.

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P98 AMINE OXIDASES BASED BIOSENSORS FOR BIOGENIC POLYAMINES DETERMINATION.

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P99 DNA-BIOSENSOR FOR Hg^{2+} DETERMINATION BASED ON POLYTHYMINE-METHYLENE BLUE MODIFIED GOLD SURFACE AND ELECTROCHEMICAL TRANSDUCTION.

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P100 DEVELOPMENT OF ELECTROCHEMICAL AFFINITY BIOSENSORS FOR THE DETECTION OF TUMOR NECROSIS FACTOR ALPHA USING DIFFERENT LIGANDS.

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P101 COMPARISON OF TWO DIFFERENT AMPEROMETRIC ENZYME SENSORS FOR ETHANOL DETERMINATION IN ALCOHOLIC BEVERAGES.

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P102 ELECTROSYNTHESIS OF ZINC OXIDE NANOPARTICLES AS PROMISING MATERIAL FOR SENSING APPLICATIONS.

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P103 COMMERCIALLY AVAILABLE EDIBLE JELLY AS A NOVEL DIELECTRIC FOR ORGANIC THIN FILM TRANSISTORS.

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P104 DETECTION OF SPECIFIC IgE TO G5 AND D2 AEROALLERGENS THROUGH AN ELIME ASSAY.

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P105 REPORTING ANALYTICAL PERFORMANCES OF ELECTROCHEMICAL SENSORS. SOME SUGGESTIONS.

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P106 ELECTROANALYSIS OF NITRATE WITH ENSEMBLES OF COPPER NANOWIRE ELECTRODES.

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P107 TOWARDS FORENSIC ANALYSIS: ADSORBITIVE STRIPPING DETERMINATION OF LSD.

D. Merli, D. Zamboni, S. Protti, M. Pesavento, A. Profumo

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P108 TBSENSE - POINT OF CARE DEVICE FOR TUBERCULOSIS DETECTION.

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P109 SENSITIVE AND INTERFERENCE-FREE GLUTAMATE AMPEROMETRIC BIOSENSOR FOR THE MONITORING OF FOODSTUFFS.

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P110 ELECTROCHEMICAL IMPEDANCE CHARACTERIZATION AND FT-IR ANALYSES OF ANTICORROSION SILICONEPOXY HYBRID SYSTEM COATINGS.

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P111 OXYGEN TRANSFER IN A GAS-LIQUID SYSTEM: KINETIC INFLUENCE OF WATER SALINITY.

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P112 SPECTROSCOPIC CHARACTERIZATION OF CADMIUM AND COPPER MODIFIED SMECTITES FOR SOIL REMEDIATION

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Plenary lectures

PL01 NEURAL INTERFACES: FROM HYBRID CHIPS TO NEURAL PROSTHESIS

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The brain is still considered the best performing computational device. It exhibits a highly complex, hierarchic organization, input integration, parallel computation, emergent properties, and functional and structural adaptation. This has greatly stimulated the attempts to create bio-hybrid/biomimetic devices in which brain tissue is interfaced with electronic chips. We focused our attention on the optimization of the cell-solid state interaction, in order to achieve long-lasting conditions of cell survival and an optimal transfer of forward and backward signals from neurons to the solid-state device. We recently generated architecture-controlled neuronal networks on microelectrode arrays, characterized their morphological and physiological properties and positioned neurons on electrode sites for improving neuro-electrode coupling. We also developed novel neuroelectronic interfaces based on micro/nano-fabrication technologies to study neuronal activity with a very high temporal and spatial resolution. Finally, we successfully interfaced organic electronics with neural tissue. We have exploited an organic photovoltaic blend for neuronal stimulation via a photo-excitation process. The use of an organic film made of a single-component (P3HT) or a donor-acceptor blend (P3HT:PCBM) is able to trigger neuronal firing upon illumination at high temporal and spatial resulution. Moreover, we have demonstrated that this bio-organic interface restores light sensitivity in explants of rat retinas with light-induced photoreceptor degeneration. These findings suggest that bio-organic hybrid opto-neural interfaces can play an important future role in sub-retinal prosthetic implants.

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Ghezzi et al. Nat Phot 7, 407 (2013).

PL02 ANALYTICAL CHEMISTRY BEYOND CHEMICAL ANALYSIS

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In the last decade the ever increasing production of high quality data from a variety of analytical platforms has had a major impact on science. It has even led to a paradigm shift in scientific research. The scale of information generation is now so great that science has to adapt or drown in a data deluge. As a result a so-called "data driven" research approach emerged as a new and powerful science paradigm. Data analytical techniques or chemometrics have become crucial scientific methods in modern science. Complex and comprehensive chemical analysis combined with powerful datanalysis obtains a crucial role in scientific research of the coming years.
The omics research is a good example where the combination of chemometrics with chemical analysis is crucial. In this lecture the results of a collaborative study on biomarker discovery for Central Nervous System (CNS) Diseases in Cerebro Spinal Fluid (CSF). Since the CSF is the biofluid in closest connection with the brains it can be expected to reflect best the biochemical status of the CNS. A comprehensive chemical analysis of the CSF may provide insights in complex brain diseases such as Multiple sclerosis. Since no analytical platform on its own yields a comprehensive image of the biochemical status several platforms (^{1}H NuclearMagnetic Resonance (^{1}H -NMR) spectroscopy, Gas Chromatography coupled with MassSpectrometry (GC-MS) and Liquid Chromatography coupled with Mass Spectrometry (LC-MS)) were investigated. The analysis of this kind of combined datasets, also called data fusion, is a challenging task. The results for a preclinical (animal) study as well as for a human dataset will be presented in the lecture

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PL03 TRACE ELEMENT SPECIATION FOR ENVIRONMENT, FOOD AND HEALTH

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Trace elements play important and varied roles in many aspects of environmental and human health ranging from essentiality to toxicity. Integral to the environmental behavior and effects of trace elements is the chemical form in which they occur. The various species of a single trace element such as mercury or arsenic can behave very differently in the environment and can elicit totally different toxic effects. Thus, in order to provide data required for risk assessment in many studies, the analytical chemist is often asked to develop analyses that can provide information on the chemical species present in samples. These analytical methods are generally referred to as speciation analysis. For trace elements, the three main methods of speciation analysis are electrochemical methods, such as anodic stripping voltammetry, X-ray spectroscopic techniques such as XANES and EXAFS, or methods based on chromatography coupled to detectors that can be element selective (AAS, AFS, plasma mass spectrometry) or molecule selective (electrospray mass spectrometry).

The methods based on chromatography/mass spectrometry are most commonly used in the area of environment, food and health. Applications of this speciation analysis method will be presented with some general examples presented along with some specific examples of recent work performed in our laboratory in Graz dealing with species of arsenic, selenium and cadmium.

PL04 SIMPLE AND EFFICIENT NANOBIOSENSING DEVICES USING PLASTIC AND PAPER BASED PLATFORMS

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The need for point of care diagnostic tests has increased enormously in the last years. Nanomaterials (i.e. nanoparticles, nanotubes, graphene etc.) thanks to their optical and electrochemical properties are bringing significant advantages in the design and application of novel biosensing systems with interest for diagnostics and other sensing applications. Nanomaterials-based biosensors, known also as nanobiosensors, are shown to be excellent alternatives for such applications. Nanobiosensors seem to be efficient, fast, low-cost and user-friendly analytical devices. Several examples related to DNA, protein, cancer cells or contaminants detections based on the use of nonomaterials will be described. The developed devices use simple and low cost platforms, both plastics and paper, easy to be handled in point of care sensing and diagnostics. They take advantages of both enhanced electrochemical (i.e. electrocatalytic) or optical (i.e. light absorbance) properties of nanomaterials. In addition lab-on-a-chip platforms that integrate nanomaterials either as detector phase or as signaling labels to achieve very low detection limits with interest for diagnostics or environment monitoring have been developed. Finally some applications of micro/nanomotors as tools to enhance the performance of biosensing technologies will also be shown.

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Keynote

K01 GREENING UNIVERSITY

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The UN [1] and UNESCO [2] have highlighted the importance and the role of school education for sustainability by declaring the decade from 2005 to 2015 dedicated to education for sustainable development with the aim to "integrate the principles, the values and practices of sustainable development into all aspects of education and learning". Many nations have taken actions to sustainability education of students [3]. Ban Ki Moon explicitly is promoting a Sustainable Development Solution Network, SDSN, of the Universities for the agenda 2015-30 [4].
Switch from a consumer culture to sustainability by adopting policies, is now a compelling need but also a tremendous opportunity for innovation. Put sustainability as the backbone of research, but also for the training and administrative procedures within the University and schools is a mandatory requirement for universities.
This paper describes two projects, the first of sustainable campus within the university and the second a series of coordinated actions directed to teaching of sustainability in schools.
The first project - "Sustainable Campus" [5] - developed at the University of Ferrara consists in a specific portal that summarizes all activities that are related to the concept of sustainability, with a specific path that leads students in the course of his career. Virtual library, manuals of sustainability and easy access to the portals for the evaluation of the various foot prints (ecological, carbon and water) and awards are available.
The project TESSI, Teaching Sustainability across Italy and Slovenia is a multitask educational project addressed to high schools [6] consisting in the organization of courses for teachers, competitions for sustainability projects (schools, student groups, individual students) and other actions (multimedia show). A manual of good education to the use of water resources was produced.
Finally the need of a renewal of Chemistry Curricula in the direction of implementing sustainability concepts will be discussed.

[1] http://www.un-documents.net/a57r254.htm
[2] http://www.unescodess.it
[3] http://www.sustainablecampus.org/universities.html
[4] http://unsdsn.org/
[5] http://sostenibile.unife.it/
[6] http://www.tessischool.eu/

Oral Communications

O01 - OFET DEVICES: A NEW STRATEGY FOR LABEL-FREE ELECTRONIC BIOSENSORS DEVELOPMENT

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Organic thin–film transistors (OFETs) present interesting features to be successfully employed as electronic biosensors, as long as their field-effect transport is directly coupled to a bio-recognition process. These devices have been already demonstrated to deliver amplified electronic responses along with the capability to operate as label-free systems. The sensor selectivity is assured by the integrated biorecognition elements that are capable to retain their bio-activity. Last but not least, they are particularly suited for on line (electronic) monitoring and they can operate in the sub volt regime. OFET devices including a Functional Biological Interlayer (FBI-OFET) were recently proposed by our group. These devices comprise a biological layer, acting as biosensor recognition element, which is fully integrated into the device structure, residing underneath the organic semiconductor film, right at the interface were the OFET two-dimensional transport occurs.[1] The platform bench-tests involved phospholipids and bacteriorhodopsin integrating OFETs exposed to 1-5% anesthetic doses that reveal drug-induced membrane changes.[2] Furthermore, a streptavidin embedding OFET was used for label-free biotin electronic detection. This device configuration besides allowing very low detection limits (few part per trillion concentration range) is also highly specific as proven by several control experiments.[3] In this presentation the features of this novel approach along with a physical modelling useful to explain the sensing device mechanism will be discussed. Specifically, in addition to a systematic investigation of the measured responses, the current-voltage characteristics of streptavidin embedding FBI-OFET have been calculated starting with the equation of conventional enhancement mode p-channel MOS-FET, but assuming a gate voltage dependence of mobility and threshold voltage and adding a constant term to model the leakage current. The calculated current-voltage characteristics are compared with the experimental data.

[1] M.D. Angione et al. PNAS April 24, 2012 vol. 109 no. 17 6429-6434.
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[3] M. Magliulo et al. Analytical Chemistry, 2013, 85 (8), pp 3849–3857.

O02 - THERMODYNAMIC BASIS FOR ENGINEERING HIGH AFFINITY AND HIGH SPECIFICITY BINDING-INDUCED CLAMP SWITCHES

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Receptors undergoing binding-induced conformational changes are used extensively by nature for the selective and sensitive detection of specific inputs and the subsequent transduction of such recognition into useful outputs. Inspired by the efficiency of these naturally occurring, binding-induced molecular receptors, researchers have recently started to exploit similar biomolecular switches in artificial biotechnologies ranging from diagnostics and imaging, to synthetic biology. DNA switches, for example, are becoming increasingly important in the fabrication of nanomachines, nanosystems and molecular computers that respond quantitatively to appropriate molecular inputs. One of the strategies exploited by Nature to build binding-induced molecular switches, which has not received much attention from the bio-engineer community, is to design a clamp-like mechanism that employs two recognition elements that simultaneously embrace a single copy of the target. It has been suggested that this strategy would lead to improved affinity and specificity. Here we use a model DNA system to dissect the thermodynamic basis by which these *clamp-based* molecular switches work. By doing so we quantify the extent with which this strategy enhances both the affinity and specificity of a single receptor. Our results have significant implications in the sensing and therapeutic fields (PCR, in vivo imaging of small repeats, interfering DNAs) and should, in addition, greatly enhance our ability to build switchable DNA nanostructures, such as DNA nanomachines and DNA with improved structural and temporal control.

O03 - SURFACE PLASMON RESONANCE IMAGING AND HUMAN DNA: HIGH SENSITIVE DETECTION AND POLYMORPHISM DISCRIMINATION

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Surface Plasmon Resonance (SPR) and its advance equipped with imaging (SPRi) are powerful tools for simple, fast, chip and multi-analyte nucleic acid detection [1-2].
In this study a DNA sensor based on SPRi was developed for the direct detection of human DNA samples (extracted from lymphocytes) and for the Single Nucleotide Polymorphisms (SNPs) discrimination.
In particular our strategy was developed around the rs1045642 SNP on the ABCB1 gene, taken as target for its potential relevance in diagnostics and in the treatment of pain therapy [3].
First pre-analytical step, based on controlled genomic DNA fragmentation with ultrasounds and thermal denaturation, was tuned.
Then analytical phase was optimized in terms of assay design: best performing probes were chosen *in silico* and then applied in a sandwich-like assay for ultrasensitive direct detection of human DNA down to a concentration of 140 aM [4].
In a further step the same assay was rationally modified, in terms of probe length and labeling, for the discrimination of SNP in whole human genome matrix, quantitatively and randomly enriched by using a non-conventional amplification i.e. Whole Genome Amplification (WGA) [5].
Finally the strategy was successfully applied for the SNP discrimination on unamplified genomic DNA extracted from lymphocytes.

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O04 - ENHANCING THE SENSITIVITY OF LATERAL FLOW IMMUNOASSAY WITH SILVER NANOPARTICLE AND FLUORESCENT SEMICONDUCTOR NANOCRYSTAL (QUANTUM DOTS) PROBES

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Lateral flow immunoassay (LFIA), known for a long time in clinical diagnostics, combines a series of benefits, including extreme simplicity, rapidity, and cost effectiveness, which makes it ideally suited for screening large number of samples and being operated outside the laboratory. Therefore, it is attracting increasing scientific and industrial interest to set rapid and portable assays for the detection of diverse compounds in numerous fields of application, among which environmental analysis, forensic science, food safety, biodefense, and space exploration. A standard LFIA device comprises: a migration membrane onto which immunoreagents are immobilized in reactive zones; a reporter probe capable of interacting with the membrane-linked reagents and providing some detectable response; additional components to make the system self-sufficient. Although several labels have been proposed to serve as reporters in LFIAs, gold nanoparticles (AuNPs) have long been used for the purpose, because of their distinguished features (such as: ease of preparation, capability to adsorb proteins, and detectability to the naked eye). Nevertheless, the growth of LFIA applications increasingly demands sensitivity improvement (especially for low-molecular-mass analytes) and the conversion of visually evaluated yes/no assays into nonsubjective quantitative tests.
Two strategies based on the use of non-gold reporters (Ag nanoparticles, and quantum dots, QDs) have first been explored and applied to develop quantitative LFIAs for measuring small molecules. The sensitivity improvement and, mostly, the better reproducibility attained through using silver nanoparticles to enhance AuNPs detectability permitted the affordable quantitation of ochratoxin A in wines and grape musts at the ng/l level.
QDs are beginning to be proposed as innovative and powerful fluorescent labels for the development of highly-sensitive, multi-analyte immunoassays [1]. Their pioneering exploitation as reporters for the development of LFIA has been investigated and proved in a model device.

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O05 - NEW ACRIDINE-CONTAINING 1,2-DIOXETANE DERIVATIVES AS PROMISING THERMOCHEMILUMINESCENT LABELS FOR BIOANALYTICAL APPLICATIONS

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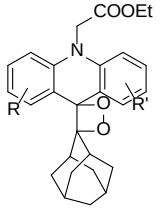
Thermochemiluminescence (TCL), i.e., the light emission originating from the thermolysis of suitable molecules (usually 1,2-dioxetanes), was proposed in the late '80s as a luminescence-based detection technique for immunoassays [1]. However, it was rapidly abandoned and replaced by other luminescence detection techniques such as photo-, bio-, chemi-, and electrochemiluminescence. Nevertheless, TCL still offers interesting and largely unexplored analytical opportunities, including the possibility to perform ultrasensitive reagent-free detection.
We recently reported an efficient synthesis of an acridine-containing 1,2-dioxetane with a relatively low light emission triggering temperature (<100 °C) and its inclusion into silica nanoparticles [2]. To further improve the performances of this TCL substrate, we designed suitable structural modifications in order to decrease the emission triggering temperature and produce more efficient fluorophores in the singlet excited state. In particular, we synthesized a library of mono-, di-, tri-, and tetramethyl substituted compounds (see scheme). The compounds were characterized from a photophysical point of view and for their potential application as TCL labels in bioanalytical techniques, obtaining LOD values ranging from 510 to 186 pmol μL^{-1}.



1 R = 1-Me, R' = H
2 R = 2-Me, R' = H
3 R = 3-Me, R' = H
4 R = 4-Me, R' = H
5 R = 2-Me, R' = 7-Me
6 R = 1-Me, R' = 5-Me
7 R = 2,3-diMe, R' = 7-Me
8 R = 1,2-diMe, R' = 7-Me
9 R = 2,3-diMe, R' = 6,7-diMe
10 R = 1,2-diMe, R' = 6,7-diMe

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O06 - NEW APTASENSORS FOR EARLY DIAGNOSIS OF BREAST CANCER

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The cancer biomarker detection aids an early diagnosis and monitor disease progression. However, rapid detection of low abundance biomarkers from the complex biological samples under clinically relevant conditions is extremely difficult, and it requires the development of ultrasensitive, robust and high throughput technological platform. In order to overcome several technical limitations associated with sensitivity, dynamic range, detection time and multiplexing, there has been great interest in applying nanomaterials-based electrochemical biosensors for the sensitive detection of biomolecules. Among the nanomaterial, gold nanoparticles (AuNPs) are considered as promising nanomaterials for sensor technology due to their high signal enhancement capability. The increasing of the area/volume relationship and consequently the attached bioreceptor on the nanostructured surface improves the sensor response. In addition, gold surface can be easily modified by thiol-ended molecules, which makes then suitable for many different biological assemblies. In this work, two aptasensors based on gold nanoparticles for the detection of Human Epidermal Growth Factor Receptor 2 (HER2) and Vascular Endothelial Growth Factor (VEGF) cancer biomarkers were proposed. Gold-nanoparticles (AuNPs) were first electrodeposed on the surface of graphite screen-printed electrode through cyclic voltammetry. Then, the gold nanostructured screen-printed electrodes were functionalized with aptamers. Different strategies, such as label-free or sandwich based assays, were studied and optimized. Calibration curves for HER2 and VEGF were obtained using Electrochemical Impedance Spectroscopy (EIS) and Differential Pulse Voltammetry (DPV). The performance of both aptasensors in terms of sensitivity, reproducibility and selectivity were studied.

O07 - SEPARATION AND QUANTIFICATION OF PLANT SECONDARY METABOLITES AND OTHER BIOLOGICAL MOLECULES BY ADVANCED ANALYTICAL SEPARATION METHODS

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This communication reports the results of our recent studies carried out to developing methods for the separation and quantification of plant secondary metabolites and other biological molecules of agrochemical interest, either by capillary electrophoresis (CE) with UV absorbance detection or by high performance liquid chromatography (HPLC) coupled to mass spectrometry. Most of the secondary metabolites investigated are phenolic compounds, which are ubiquitous in the plant kingdom and can be found as free molecules (aglycones), in the form of conjugates (usually as glycosides) and esters, or as oligomers or polymers. Most chromatographic and electrophoretic separations of these analytes are performed in aqueous solutions whose composition is one of the main factors influencing their separation performance. This aspect is particularly relevant for a significant number of phenolic compounds bearing different concomitant functionalities, consisting of ionisable and/or hydrogen-bonding groups, hydrophobic regions, and hydrophilic moieties. Such multifunctional molecules may interact to different extents with the various components of the surrounding aqueous solution and with either the stationary phase or the capillary wall, in chromatography and in capillary electrophoresis, respectively. We illustrate and discuss a variety of factors that influence both electrophoretic and chromatographic behaviour of phenolic compounds of particular interest in plant biology and phytochemistry. The presentation evaluates the influence of the composition of either the electrolyte solution (BGE) or the mobile phase on the selective separation of representative phenolic compounds in capillary zone electrophoresis (CZE) and in reversed phase liquid chromatography (RP-HPLC), respectively. Appropriate selection of the composition of either the BGE or the mobile phase involves the evaluation of the equilibrium in solution that might take place between the analytes and the components of such solutions. The result is the possibility of tailoring selectivity and efficiency of the considered separation systems by incorporating suitable buffering agents and additives into the BGE or the mobile phase, respectively. Practical applications of these approaches to separation and quantification of phenolic compounds in different plant matrices are then discussed.

O08 - INNOVATIVE CAPILLARY ELECTROPHORESIS METHOD DEVELOPMENT FOR THE DETERMINATION OF ALMOTRIPTAN AND ITS IMPURITIES: QUALITY BY DESIGN APPROACH

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Quality by Design (QbD) principles have been adopted by pharmaceutical industries with the aim of improving the understanding of processes and products and thus improving product quality and regulatory flexibility [1]. A key component of QbD is Design Space (DS), defined as the multidimensional combination of the input variables where the assurance of quality is provided. QbD has been recently attracting attention in the development of analytical separation methods [2].
The aim of this study is the application of QbD approach in the development of a capillary electrophoresis (CE) method for the simultaneous determination of almotriptan, used for the acute treatment of migraine attacks, and its main impurities. The analytical target profile of the method was the baseline separation of all the peaks, with LOQ values for the impurities equal to or lower than 0.1% with respect to the active pharmaceutical ingredient. Control quality attributes (CQAs) were defined as resolution values of critical peak pairs and analysis time. A scouting study including several CE operative modes was carried out, and microemulsion electrokinetic chromatography (MEEKC) led to the best results. In MEEKC the background electrolyte is a microemulsion, which is a stable system containing oil and water, stabilized by a surfactant and a co-surfactant. The performance of the MEEKC run depends both on the proportions of mixture components (MCs) of the microemulsion and on the values of process variables (PVs). Knowledge space on the PVs was investigated by means of an asymmetric screening matrix. Then, a mixture-process variable approach, which simultaneously varies MCs and PVs, was applied. Monte-Carlo simulations were performed to include uncertainty of the parameters of the models and to estimate the probability of meeting the specifications imposed on the CQAs, and allowed the DS to be defined by means of risk of failure maps. Finally, a control strategy based on system suitability tests was implemented.

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O09 - ON-LINE SPE-LC-MS/MS ANALYSIS OF SELECTED ENDOCRINE DISRUPTOR COMPOUNDS (EDCs) IN SURFACE WATER AND WASTEWATER SAMPLES IN ITALY

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Mass spectrometry coupled to liquid chromatography (LC-MS) is nowadays a key technology for many applications. With regard to environmental applications, the need of increasing the capabilities and performances of this tool is driving new strategies and instrument advances.
This study focused on the development of analytical methods for the determination of EDCs in surface water and wastewater. Referring to these matrixes, the main problems to be solved are the presence of very low concentration levels of target analytes in complex matrixes, together with the necessity of the reliable identification and confirmation of the environmental contaminant occurrence, as defined by EU Decision 2002/657/EC. Within this topic, the quantitative analysis of estrogens in surface water and wastewater has been recently carried out [1], employing a triple quadrupole working in Multiple Reaction Monitoring mode (MRM) with an ESI interface operating in negative ion mode; the up to date strategy of on-line pre-concentration of the sample was adopted in order to minimize matrix effect, as well as for maximizing sensitivity and method throughput.
The method showed a very good linearity from 250 ng/L down to compound specific quantification limits, which were included between 0.25 and 2.00 ng/L. The method reliability was tested on different kinds of real samples spiked with estrogens, obtaining recoveries included between 71% and 95% with a total run time of 10 minutes.
Currently, we are expanding our method to the determination of octyl and nonylphenols, and ethoxylate oligomers with 1-3 ethoxylic units through a same LC-ESI-MS/MS analysis that includes both ionization modes; in fact, this approach is currently reported in only one literature study [2]. These compounds are persistent metabolites in the aquatic environment deriving from alkylphenols polyethoxylates, largely employed as non-ionic surfactants in several industrial applications until their use was restricted by the Directive 2003/53/EC. This topic is still of current concern since the restrictions do not cover the use of pretreated goods imported from outside of the EU.

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O10 - MOLECULARLY IMPRINTED BEADS FROM SACRIFICIAL POROUS SILICA: SYNTHESIS, PROPERTIES AND ANALYTICAL APPLICATIONS

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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, it shows many practical drawbacks, such as large losses of imprinted material as submicrometer dust, limited solubility of template molecules in the porogenic solvents and morphological heterogeneity of the crushed materials.
With the purpose of overcoming these drawbacks, several alternative approaches based on the synthesis of imprinted beads have been proposed in recent years. The main advantages of such approaches consist in the easy preparation of spherical imprinted polymeric particles with narrow diameter and pore size distribution, particularly indicated for separative applications such as liquid chromatography and solid phase extraction.
In this field, one of the most interesting methodologies consists in filling the pores of meso- or macroporous silica beads with an imprinting mixture, polymerizing it and dissolving the inorganic support by corrosion with hydrofluoric acid or ammonium fluoride, leaving porous imprinted beads as a negative image of the sacrificial silica beads. Templates can be introduced within the silica beads together with the pre-polymerization mixture or previously covalently grafted to the inner surface of the pores.
In this communication we describe the effect of silica porosity, pore surface pre-treatment, presence of a porogenic solvent and polymerization conditions on the binding performances of the imprinted polymers with molecular recognition properties towards steroids, antibiotics, peptides and natural products. The influence of the template grafting on the selectivity of the imprinted polymer is also reported.
The use of sacrificial silica beads as microvessels for the synthesis of molecularly imprinted beads results to be an efficient alternative to emulsion, precipitation or bulk polymerization. It is particularly convenient when a fragmental or mimic template approach is needed or when compatibility between template molecule and porogenic solvent does not exist.

O11 - GAS CHROMATOGRAPHIC APPROACHES FOR THE DETERMINATION OF NEW MARKERS OF CELLULOSE DEGRADATION IN INSULATING MINERAL OILS OF POWER TRANSFORMERS

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Thermal degradation of solid insulating, i.e. Kraft paper, hampers the correct working conditions of power transformers, causing failures and accidents of both social and environmental impact.Markers usually accepted to evaluate degradation of paper are the presence ofCO, CO_2 and 2-furaldehyde in oil. Since they can be originated even by natural ageing processes of the oil, their identification cannot give univocal information.
The presence of methanol and ethanol in transformer oils has been recently correlated to thermal degradation of solid insulating. Methanol and ethanol originate only from paper degradation.Since at equal life times of electric transformers, they develop in larger quantities than traditionally used markers, their quantification in oils is potentially easier.
In this work, analytical procedures for the determination of CH_3OH and C_2H_5OH in insulating oils, were developed. Head space gas-chromatographic methods using flame ionization (HS-GC-FID) and mass spectrometer (HS-GC-MS) detectors were comparedto quantify the two markers in oil.The best operative conditions were obtained optimizing the sample preparation methodology, and some GC parameters (split ratio, injection volume, head space temperature and ramp elution).For both the methods, linearity was in the range 20-3000 ng/g. Detection limits of CH_3OHwere 12 ng/g (HS-GC-FID) and 1.3 ng/g (HS-GC-MS), while for C_2H_5OHthey were 27 ng/g (HS-GC-FID) and 3.1 ng/g (HS-GC-MS). Repeatability was evaluated analyzing oils sampled from in-service transformers. The accuracy of both methods was verified by a proficiency test (Cigré JWG A2/D1.46).Finally,twenty-one in-service oils from field transformer samples were analyzed.The results obtained, compared by a one-sided paired t-test, confirmed that the two methods are not statistically different.For each sample, $CH_3OH$and C_2H_5OHcontent was correlated with the years of transformer activity.
Both the methods allow reliable identificationof $CH_3OH$and C_2H_5OH in oils, improving the monitoring activities of transformers. Although HS-GC-MS allows to obtain slightly better detection limits, HS-GC-FID is a preferable tool, due to its less expensive instrumentation.

O12 - HEADSPACE SOLID-PHASE MICROEXTRACTION ANALYSIS OF SHORT CHAIN FATTY ACIDS IN FAECAL SAMPLES: APPLICATION TO COMPARATIVE METABOLOMIC STUDIES OF THE HUMAN GUT MICROBIOTA

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The composition and activity of gut microbiota coevolve with the host from birth through the entire lifespan and it is subject to a complex interplay that depends on the host genome, nutrition, and life-style [1]. The mutually beneficial relationship between the host and its resident gut microbiota relies on the production of microbial metabolites, as short chain fatty acids (SCFAs). Reflecting the end point of bacterium fermentation in the colon, SCFAs provide a relevant contribution to the host's nutritional, immunological and physiological status.
Their analysis in faeces is problematic [2], and requires time consuming and different steps procedure. In this communication a simple and fast method, based on headspace solid-phase microextraction (HS-SPME) of acidic extract of faecal samples, is presented. Quantitation of four SCFAs (acetic, propionic, butyric and valeric acid) was performed showing good repeatability and sensitivity, with values of CV% for intra-day and inter-day repeatability less than 10% and 14% respectively, and LOD at nmol/g concentration level.
The developed methodology was applied to comparative metabolomic studies of gut microbiota in a wide range of case studies involving human subjects.

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O13 - DETERMINATION OF ANTICOAGULANT DRUGS AND THEIR METABOLITES IN ORAL FLUID AND PLASMA SAMPLES BY HPLC-FLUORIMETRY

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Warfarin is the most common anticoagulant drug prescribed for the treatment of many diseases. It is metabolized by the cytochrome P450 to inactive hydroxylated metabolites and by ketone reductases to warfarin alcohols, which show a little anticoagulant activity. The large number of factors that may interact with this therapy (diet, comorbidities, other drugs, etc.) makes it relatively easy to go out of the optimal range. The standardized evaluation of the coagulation time (international normalized ratio, INR), which requires blood sampling, is the primary assay used in monitoring warfarin therapy. The determination of warfarin and warfarin alcohols in oral fluid samples could offer an alternative approach to INR assay, because the oral fluid concentration of warfarin is expected to mirror the concentration of the unbound warfarin in plasma (i.e. the pharmacologically active fraction, about 1%) and could anticipate the INR variations, thus allowing a more effective prevention of adverse events.
In this study analytical procedures were developed for the determination of both total content and unbound fraction of warfarin and warfarin alcohols in oral fluid and plasma samples by HPLC-fluorimetry. Fluorescence detection was performed at 390 nm (excitation wavelength 310 nm). LODs for warfarin and warfarin alcohols were 0.2 and 0.1 ng/mL, respectively, recoveries ranged between 90% and 70%, and intra- and inter-day precisions were <10% (RSD) for all methods. The correlations between oral fluid and plasmatic (total and unbound) levels of warfarin and warfarin alcohols, and between these concentrations and INR were preliminary evaluated in a longitudinal study involving 10 patients.

O14 - ELECTROCHEMICAL IMMUNOASSAY FOR SCREENING OF CELIAC DISEASE IN SALIVA

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Celiac Disease (CD) is a gluten-induced autoimmune enteropathy found in genetically susceptible subjects. It is one of the most common immune-mediated diseases in Europe and North America with a high number of undetected cases. Thus, the development of rapid, cheap and simple screening methods is highly needed in order to prevent negative outcomes for untreated patients (several chronic or malignant diseases). Currently, CD diagnosis involves the detection of anti-transglutaminase IgA antibodies (anti-tTG IgA) in blood serum through the use of ELISA systems, confirmed by histology of the intestinal mucosa. In this work we developed an electrochemical immunosystem for the determination of anti-tTG IgA in saliva samples, which are easily obtained by non-invasive techniques. In this matrix, only a RIA method has been successfully utilized in CD screening of about 6000 primary school children (1). The proposed system can be an alternative for preliminary screening diagnosis even in "Doctor office" or in non-hospital facilities, becoming a "point of care testing" (POCT).
The method, an ELIME (Enzyme-Linked-Immuno-Magnetic-Electrochemical) assay, is based on the use of magnetic beads as support for the immunological chain tTG/anti-tTG IgA/anti-human IgA-AP, coupled with an array of 8 magnetized screen printed sensors localized at the bottom of 8 wells, this latter connected to a portable potentiostat.
To overcome problems related to the low concentration of IgA in saliva and to the high viscosity of this medium, a high sensitivity protocol has been optimized evaluating the appropriate blocking agent, washing solution and diluents for saliva samples and for anti-human IgA-AP.
Currently the optimized method is undergoing validation with blind analysis of 100 saliva samples obtained and separately tested by the University Hospital of Rome La Sapienza with RIA method. The excellent concordance of the first 50 samples shows that is possible to detect salivary tTG-Abs in CD patients with a rapid, non-invasive, simple, reproducible and sensitive method.

O15 - HUMAN BLOOD MICROPARTICLES AND PLATELETS: A COMPARATIVE PHOSPHOLIPIDOMIC INVESTIGATION BY HYDROPHYLIC INTERACTION LIQUID CHROMATOGRAPHY-ELECTROSPRAY IONIZATION MASS SPECTROMETRY

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Blood microparticles (MP) represent the most important class of the so called *cellular microparticles*, sub-micrometric vesicles commonly released from every type of human cell. Blood MPs play an important role both in physiological processes, like haemostasis, and in several acute or chronic pathological states, including haemolysis, anemia, inflammation, atherosclerosis, type-2 diabetes mellitus and cardiovascular diseases [1]. Among blood cellular bodies, platelets have been recognized as the main source of MPs, accounting for more than the 70% of the total population [2]. The relationship between blood MPs and platelets has been confirmed by a recent investigation performed in our laboratories on their phospholipidomes, based on the hyphenation between hydrophilic interaction liquid chromatography (HILIC) and electrospray ionization mass spectrometry (ESI-MS) [3]. Although the same set of phospholipids (PL), consisting in 131 species divided into seven different classes, was identified in blood MP and platelet samples obtained from the same healthy donors, significant differences in terms of phospholipid distribution were observed.
The present communication will focus on the differentiation between the phospholipidomes of blood MPs and platelets on a quantitative basis. The variations occurring in the distribution of PLs belonging to specific classes and in the relative abundance of different PL classes, evaluated through HILIC-ESI-MS data, will be described in detail.

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O16 - INTERACTION BETWEEN TREHALOSE CONJUGATED β-SHEETBREAKER PEPTIDE ANDAβ(1-42) MONOMERS: INSIGHT INTO THE Aβ RECOGNITION PROCESS AND NEUROPROTECTION

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Alzheimer disease (AD) is a progressive fatal neurodegenerative disorder which is clinically characterized βy a decline of cognitive functions including memory, orientation and language. The amyloid-beta peptide (Aβ) is nowadays reported as a double-faced biomolecule which has been shown to play a crucial role in AD. Indeed, although Aβ monomers are capable of stimulating neuronal survival [1], the early soluble Aβ aggregates are toxic as they cause neuronal death. Therefore Aβ self-assembly is deleterious for two reasons: i) neurotoxic species are formed, ii) neutrophic factors are cleared. Inhibiting Aβ self-oligomerization and/or stabilizing Aβ monomers might, therefore, provide useful approaches to control the pathogenic pathways underlying AD. We have conjugated a trehalose moiety to the known β-sheet breaker pentapeptide LPFFD [2,3].
Trehalose has received a special interest because it has been found to be effective in the treatment of neurodegenerative diseases associated with peptide or protein aggregation. The glycoside moiety, which was covalently linked to the C-terminus of the amino acid sequence endows the peptide with increased resistance to proteases.
In this work we show the ESI-MS study, besides using several analytical techniques, including Analytical Ultracentrifugation (AUC), Dynamic Light Scattering (DLS) and fluorescence spectroscopy in order to investigate the amino acid region involved in the recognition process indicating a direct interaction of the studied peptide with the monomeric form of Aβ. The properties of glycoconjugates to stabilize single molecules of Aβ peptide might represent a promising strategy to halt the early stage of oligomerization and maintain the activity of Aβ monomers. This last issue is being addressed in primary neuronal cultures.

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O17 - ANALYTICAL PLATFORM FOR THE PROTEOME ANALYSIS OF NON MODEL PLANT SPECIES

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Until recently, large scale proteomic investigations in the plant field have only been possible for a few model species for which the whole genome sequence had been fully determined [1]. The proteomic analysis of non model plant poses two major difficulties: to begin with, because of the complexity of the matrices examined, it is difficult to obtain high quality protein extracts, and secondly, due to the lack of sequenced genomes, the database information available is limited.
The main aim of this work was to establish an effective analytic platform for the isolation of olive pulp and pomegranate proteins to provide an effective method for the identification of as many proteins present in these samples as possible. More specifically, for the olive pulp we proposed two different extraction protocols for gel-free approaches, using physiological (CHAPS buffer) and denaturing (SDS buffer) conditions and two precipitation strategies were tested for each one. Extraction of pomegranate proteins was performed using only denaturing conditions and enrichment by ProteoMiner ligand libraries, which act via bioaffinity recognition and “normalize” the dynamic range of the sample under overloading conditions, thus enhancing very low-abundance protein isolation [2]. In both cases, the extracted proteins were trypsin digested, and the resulting peptide mixture analyzed by reversed-phase (RP) nanoHPLC-tandem MS (MS/MS). Different protein databases, in particular *Viridiplantae* entries for SwissProt and NCBI, and TAIR10, were used. Thus the choice of different databases for MS/MS spectra search and peptide and protein identification was made in order to provide a platform which would allow an increase in the number of protein identifications, also by homology, thus providing a more complete description of the proteome of non model plants. The olive pulp results showed that the SDS and CHAPS extractions, when associated to two different precipitations, permitted the extraction of different proteins on the basis of different solubility properties. The pomegranate results highlighted that the ProteoMiner enrichment was effective for low-abundance proteins isolation. The use of selective extraction protocols, advanced MS techniques in combination with three databases allowed us to identify more than 1000 proteins both for the olive pulp to the pomegranate.

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O18 - PROTEIN LABBELING BY P-HYDROXY-MERCURY-BENZOATE: A LOW COST PROTEOMICS

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Chemical labelling in combination with mass spectrometry is appointed as a modern approach for quantifying biopolymers, especially proteins. Protein labelling approaches are generally based on elemental mass spectrometry techniques, specifically inductively coupled plasma-mass spectrometry (ICP-MS). In this work we present a novel method for the characterization and determination of proteins labelled with p-hydroxymercurybenzoate (pHMB, an organic mercury species widely used for mercaptan and thiolic compound labelling), based on the on line oxidation of pHMB-labelled proteins with a novel on-line UV/microwave (MW) photochemical reactor, followed by cold vapour generation atomic fluorescence spectrometry (CVG-AFS) detection. MW/UV process leaded to the quantitative conversion of pHMB and protein-pHMB bioconjugates to Hg(II), with a yield of 89±0.5% without using chemical oxidating reagents and avoiding the use of toxic carcinogenic compounds. LC-MW/UV-CVGAFS method has been applied to the characterization, separation and determination of several thiolic proteins (albumins, beta-lactoglobulin and k-casein) using SEC and RPC. Several denaturation systems (8 M urea, 3 M GdnSCN, 6 M GdnHCl, 0.2% SDS, 20% methanol, 50% trifluoroethanol) have been employed to study pHMB-ovalbumin bioconjugates, using ovalbumin as a model protein. The maximum number of titrated SH- groups for OVA has been obtained denaturing the protein with 0.2% SDS at room temperature (2.7 ±0.3 SH- groups). The kinetics of the binding of pHMB with OVA was also investigated. SEC-MW/UV-CVGAFS was also been applied to the study of thiolic proteins in raw matrices such as human plasma, human saliva and milk, in order to demonstrate the analytical performance of this technique in the study of real samples. Due to the well assessed role of thiolic proteins in physio-pathology this methodology could allow a preliminary screening to identify unique markers of oxidative stress. The potentialities of RPC-MW/UV-CVGAFS were explored for the study thiolic fragments in triptic digests and the effect of ageing on OVA in aqueous extracts of fresh and aged OVA-cinnabar paint replicas. The aim of this part of the work was to show how RPC-MW/UV-CVG-AFS system coupled to pHMB labeling i) could be applied to identify CYS containing peptides, ii) could be employed to identify species-specific proteins from the chromatographic elution pattern.

O19 - ASSESSMENT OF INNOVATIVE TECHNIQUES FOR RESTORATION

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A novel class of gel-like materials is presented as low impact cleaning tools for the treatment of the surface of carbonatic stones affected by the detrimental presence of sulphates and oxalates. They are Highly Viscous Polymeric Dispersions (HVPD) based on a tridimensional network of PolyVinyl Alcohol (PVA) covalently cross-linked by borax [1-3].
The formation of calcium sulphate (gypsum) and oxalate (weddellite) patinas was opportunely induced onto the surface of some travertine specimens. Thereafter, some cleaning test have been carried out by means of HVPDs doped with different additives (e.g. ammonium carbonate, EDTA, sodium citrate and ammonia). In order to quantitatively evaluate their efficacy in treatment of the patinas, Ion Chromatography analyses were performed to determine the concentration of sulphate and oxalate removed by the HVPDs. The results show that ammonium carbonate, EDTA and ammonia are highly effective in removal weddellite and gypsum.
The treatment method assessed in this study has been successfully tested on the Vecchietta's wall paintings affected by gypsum in the Old Sacristy of Santa Maria della Scala in Siena. [4]

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O20 - IRON GALL INKS: IS COPPER A KEY ELEMENT FOR HISTORICAL AND ARCHAEOMETRIC INFORMATION ON MEDIOEVAL MANUSCRIPTS? AN APPLIED RESEARCH FOCUSED ON GUARNERIO D'ARTEGNA (1410-1466)

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Micro X-ray fluorescence (micro-XRF) is a very suitable non-destructive analytical technique for the characterization of iron gall inks (IGIs) and this work is focused on survey of ink composition of two manuscripts written by Guarnerio D'Artegna (1410-1466) during 1441-1442 and kept at the Guarneriana Library of San Daniele del Friuli (UD), the oldest library in Friuli Venezia Giulia Region and one of the first institutions of public reading in Italy.
IGIs are black inks produced using 4 basic ingredients: galls, vitriol (iron (II) sulphate), gum arabic and an aqueous media (beer or wine). From the first centuries until the 19th century the majority of manuscripts were written with these inks and it is well known that iron sulphate can be contaminated with other minor metals such as Cu, Pb or Mn. Impurities are related to the mineral composition of vitriol, while K is correlated with the organic component (i.e. gum arabic). These metals seem to be very useful for a good classification of different IGIs [1]. Their quantification obtained by means of ARTAX 200 micro-XRF spectrometer (Bruker AXS) and calculated as relative to the major element, Fe, allows to distinguish inks even on the same manuscript.
We applied this procedure to two Guarnerio's manuscripts: codex 79 and codex 71. The obtained data permit a characterization of different inks used by the author and we discovered a significant change of ink in codex 71 starting on folio 65.
An insight examination of various detectable element content allows us to conclude that copper is the most useful element for a good discrimination of IGI and our results could be used in future studies also to extract information about the authenticity of similar manuscripts.

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O21 - USE OF NANO GOLD PARTICLES OBTAINED BY LASiS FOR SEIRA AND IMMUNO-SERS ANALYSES OF HERITAGE MATERIALS

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The present research has been focused on the application of gold nanoparticles (AuNPs) obtained by laser ablation synthesis in solution (LASiS) [1] for the development of surface enhanced vibrational techniques suitable to analyze heritage materials. LASiS allows to obtain stable nanoparticles, which are charged and for this reason do not need any stabilizing molecules. Consequently, these particles can be easily functionalized without any ligand exchange reaction or extensive purification procedures. Indeed, LASiS can be considered an excellent green and cheap alternative, which allows to avoid the presence of unreacted compounds in the colloidal solutions and the formation of chemical waste. Gold nanoparticles have been used to develop Surface Enhanced Infrared Spectroscopy methods for the characterization of colorants. Analyses have been performed in reflection/ absorption mode, applying a drop containing a mixture of colorant and the Au colloidal solution on a glass slide. Results showed that thanks to the enhancement produced by the AuNPs it is possible to analyze small amount of diluted solutions of the target colorant, extracted from dyed wool. Differently, AuNPs have been used for the synthesis of new SERS label (clusters of AuNPs functionalized with a Raman-active dye) that have been used to mark antibodies for the selective location of protein in paint cross sections [3]. This approach offers the advantages of sensitive analysis and versatile functionalization of the plasmonic substrate. Moreover, the combination of immunochemical methods and Raman spectroscopy permits the simultaneous identification of the target protein as well as the Raman components.

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O22 - THE CHEMISTRY OF POLYSACCHARIDE GUMS USED AS PAINT BINDERS: ANALYTICAL PROCEDURES, INTERACTIONS AND AGEING

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Since the 3rd century BC, saccharide materials (such as plant gums, flour and honey) have been used as media for paintings, illuminated manuscripts, inks, as well as materials for restorations. The possibility of reliably identifying saccharide materials in paintings and polychromies is the object of this research. Plant gums (arabic, tragacanth, fruit tree, ghatti, guar and karaya) are natural polysaccharide materials exuded by plants or extracted from the endosperm of seeds. They are high molecular weight polymers, made up of aldopentoses, aldohexoses and uronic acids. Despite their documented use, polysaccharide materials have rarely been identified in works of art [1, 2]. In this work, two GC/MS analytical procedures for the analyses of polysaccharides were optimised and the sugar profiles obtained were compared to verify that the data were not depending on the analytical procedure. These procedures were thus used to widen the database of saccharide profiles of materials used in paintings and polychrome objects [3]. Moreover to ensure a reliable identification of a saccharide material in a painted object, the macromolecular and compositional changes taking places in polysaccharide gums as an effect of ageing and the simultaneous presence of inorganic and other organic materials were investigated by using thermoanalytical (TGA and DSC) and chromatographic techniques (GC/MS). The data were used to establish the relative stability of different monosaccharides and, thus, to build new decisional schemes for a reliable identification of a polysaccharide gum in a paint sample. These decisional schemes were finally successfully used to identify the source of saccharide materials detected in several works of art of different provenance, typology and historical period [4].

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O23 - ELECTROCHEMICAL ANALYSIS OF IMMUNOGLOBULIN-Y WITH ENSEMBLES OF NANOELECTRODES: DETECTION OF EGG-YOLK AS BINDER IN TEMPERA PAINTINGS

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A pictorial layer is a complex sample, composed by pigments kept together by a binder such as animal glue, casein, egg, drying oil, natural gum or a synthetic polymer. The tempera technique is based on the use of water dispersible binders which, upon drying, become insoluble. The classic tempera binder is egg yolk, but also whole egg or egg white, alone or mixed with flour or animal glue, were used. The identification of the binder is crucial both for authentication and conservation purposes, however, identifying proteins from different animal sources is not easy. To this aim, fluorescent and chemiluminescent immuno-sensors were recently developed to detect ovalbumin, which can be present both in egg white and yolk [1].
In order to improve the selectivity for the specific detection of egg yolk, in the present study we focus on a different analyte, that is the glycoprotein immunoglobulin IgY, present only in egg yolk. The transducers used here are the nanoelectrode ensemble (NEEs) prepared in our lab via membrane templated electroless deposition of gold [2]. Because of their geometrical and diffusion characteristics, NEEs display significantly small detection limits. An additional advantage of NEEs for biosensing purposes is the possibility of binding organic macromolecules, like proteins, onto the wide polycarbonate area which constitutes the insulating surface interposed between the nanoelectrodes of the ensemble.
To the present goal, IgY in the paint extract is, at first, captured by the NEE which is then incubated with anti-IgY-HRP, to finally record an electrocatalytic signal caused by the addition of H_2O_2 and methylene blue. The sensor shows satisfactory detection capabilities which are tested by analyzing both paint models, prepared in the lab, and real samples, from paintings of the XVIII- XX century. Multivariate exploratory analysis is applied to classify the voltammetric patterns furnished by the nanostructured biosensor, confirming its capability to differentiate egg-yolk tempera from other kind of tempera binders as well as from acrylic or oil paints.

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O24 - DEVELOPMENT OF INNOVATIVE EMBEDDING PROCEDURES FOR THE ANALYSES OF PAINT CROSS SECTIONS IN FITR MICROSCOPY

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A polychrome sample is usually formed by overlaid paint layers of different thickness (10-100 μm) applied over the support (canvas, panel or wood) and composed of mixtures of organic and inorganic materials.
The characterisation and the stratigraphical location of the different paint components is of the outmost importance both for historical studies and the identification of the most suitable conservation and restoration methodology to be adopted.
The present research focused the attention on the development of innovative embedding procedures for the analyses of paint cross sections in FTIR microscopy. This technique was chosen because it is widely employed for the characterisation and location of organic and inorganic components in artistic samples. Moreover, its performances may be critically affected by sample preparation in terms of superficial morphology and contamination from the embedding materials.
The use of IR inactive salts such as KBr and NaCl as embedding medium and of cyclododecane as a temporary barrier towards the infiltration of the resin has been discussed, considering the effects of the different methods on the results achievable by means of FTIR microscopy both in ATR and in Total Reflectance mode [1-3].

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O25 - GEOGRAPHICAL TRACEABILITY AND AUTHENTICITY OF EXTRA VIRGIN OLIVE OIL BY CHEMOMETRIC TECHNIQUES AND CHROMATOGRAPHIC FINGERPRINT

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In recent years, the identification and traceability of foods play a key role, as a defense, both for the producers and the consumers. Therefore, the necessity to develop new analytical methods that allow, a posteriori, to define the correct geographical origin, emerged. PDO Extra virgin olive oil is one of the foods made in Italy with the highest added value, because it is related to a delimited area of production. However, it is too often subjected to frauds and imitation that are difficult to detect. The aim of this work was therefore to develop a new analytical method that could allow the identification of PDO extra virgin olive oil, and in particular, which could allow to discriminate the Sabina PDO from other extra virgin olive oil. To achieve this objective, a complex chemical and chemometric analysis were carried out. At first, through an experimental design protocol, the extraction of polyphenolic components was optimized in terms of recovery, time and cost. The identification of the compounds was performed through the use of mass spectrometry. The chromatographic profile of each sample was considered as a fingerprint of olive oil. Before applying classification methods, it was necessary to pretreat the chromatographic data. For the correction of the baseline, the algorithm "Penalyzed Asymmetric Least Squares"[1] was used. After correcting the baseline, it was necessary to pretreat further chromatographic signals to ensure that the peaks of the analytes were aligned. Operatively, the alignment of the chromatograms was performed using iCoshift algorithm[2]. The chromatographic profiles of extra virgin olive oils extracts after being "pretreated", have been used as data for the construction of the classification model. Specifically, the method applied for discriminant classification was Partial Least Squares Discriminant Analysis (PLS-DA)[3]. The predictive capability of a multivariate classification model can be affected by the presence of a large number of variables, in our case, not all the points that constitute the chromatographic profile carry discriminant information, and a selection of portion of the chromatogram was necessary. For this purpose, the technique Backwards Interval PLS (Bi-PLS) coupled to a procedure based on Genetic Algorithms (GA)[4] was used. Once calibrated, the classification model (PLS-DA after Bi-PLS-GA) has been validated, and tested for its predictive capacity on external extra virgin olive oil samples and 90% of these were correctly classified. In conclusion, the analytical-method developed, being based on the chemometric processing of the results of chemical analysis on the finished product, doesn’t rely on label and can allow detecting imitations and falsifications of Sabina PDO.

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O26 - DATA FUSION APPROACH FOR THE VARIETAL CLASSIFICATION OF LAMBRUSCO P.D.O. WINES

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Owing to the increasing of the throughput of modern analytical techniques and the needs of getting exhaustive information on the peculiarities of similar samples in terms of composition for both authenticity and geographical or varietal origin purposes, it is necessary to extract hidden information from complex data set.
The possibility to jointly analyze data sets arising from different sources (e.g. different analytical determinations/platforms) allows capturing the latent information that would not be extracted by the individual analysis of each block of data. Several approaches are proposed in the literature and are generally referred to as data fusion ones. In this work a hierarchical data fusion is proposed [1,2] for the characterization of three varieties of Lambrusco Wine (Salamino di Santa Croce, Grasparossa di Castelvetro, Sorbara), a typical P.D.O. product of the District of Modena (Italy). In particular, 60 wine samples of the three different varieties were analyzed by means of HPLC-DAD fro the phenolic compounds evaluation, Emission-Excitation Fluorescence Spectroscopy and 1H-NMR.
Since the analytical outputs are characterized by different dimensionality (matrix and tensor), several multivariate analysis were applied (PCA, PARAFAC, MCR-ALS) in order to extract and merge, in a hierarchical way, the information present in each data set.
Results showed that this approach was able to well characterize Lambrusco samples giving also the possibility to understand the correlation between the source of information arising from the three analytical techniques.

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O27 - KERNEL-BASED BATCH MULTIVARIATE STATISTICAL PROCESS MONITORING: BETTER DISCRIMINATION WITH A BETTER UNDERSTANDING

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In the past decade, non-linear data analysis techniques, such as the kernel-based ones, have been widely applied in different fields especially for their capability to model complex relationships. Many variants of these methods exist, but each of them is based on a so-called kernel transformation: a kernel function is applied to the original data matrix, transforming it into a square symmetric one, whose elements represent distance measures between two observations. This actually means mapping the data in a higher dimensional feature space [1]. Hence, performing Principal Component Analysis (PCA), Partial Least Squares (PLS) or Partial Least Squares Discriminant Analysis (PLS-DA) on this matrix results in Kernel-PCA, Kernel-PLS or Kernel-PLS-DA, respectively. Even if most of the non-linear techniques provide high classification or prediction performance, they show a critical disadvantage: since the original input space is transformed by the application of the kernel function, the information related to the original variables is completely lost. In order to overcome this issue, non-linear biplots can be appealed to [2]. The key idea is to project onto the model space so-called pseudosamples which carry all their weight in one variable. Building and projecting a set of pseudosamples per each measured variable permits to reconstruct its trajectory in the model space, improving the interpretability of the outcomes obtained by using a kernel-based method. The main aim of this work is to explore the potential of these non-linear techniques for improving the fault detection in batch processes, combining Kernel-PLS-DA and three common approaches to analyse batch data by means of bilinear models: Landmark Features Extraction, Batchwise Unfolding and Variablewise Unfolding. The results show using non-linear kernel functions enhances the discrimination between NOC (Normal Operating Condition) and faulty batches with respect to the standard bilinear models. Moreover, the pseudosamples projection enables the diagnosis of the detected faults, improving the process understanding.

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[2] J.C. Gower, S.A. Harding, Biometrika 75 (1988) 445-455.

O28 - DATA REDUCTION OF HYPERSPECTRAL IMAGES

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In the context of HyperSpectral Imaging (HSI) techniques, the high dimension of data collected represents a main issue, since hyperspectral images of 50 MB each or more can be easily acquired in few seconds. When dealing with datasets composed by a wide number of samples, the compression of the useful information contained in each hyperspectral image into an optimized set of few parameter values would be therefore highly valuable. In order to significantly reduce the dataset size, a chemometric strategy derived from the colourgrams approach, already developed for the elaboration of RGB images [1], is proposed. This procedure essentially consists in compressing the useful information contained in each hypercube into a one-dimensional signal, named hyperspectrogram, which is created by combining several quantities obtained by applying PCA to the unfolded hypercube data [2]. By reducing millions of data of the original image to a vector composed by few hundreds of points, hyperspectrograms allow to simultaneously analyse up to hundreds of images, thus enabling a complete overview of each dataset and an easy identification of possible outlier samples. Indeed, hyperspectrograms can be used as a compact set of descriptors and easily subjected to common multivariate analysis methods for data exploration, classification or calibration. In addition, a further improvement both of data compression and of calibration/classification performances can be obtained by applying a proper variable selection method to the hyperspectrograms dataset. A visual evaluation of the correctness of the choices made by the feature selection algorithm can be achieved by representing the selected spatial features back into the original image domain. Likewise, the interpretation of the chemical information underlying the selected regions of the hyperspectrograms related to the loadings is enabled by projecting them in the original spectral domain. Examples of applications of the hyperspectrogram-based approach to calibration and defect identification issues on food samples demonstrate the effectiveness of the proposed procedure.

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O29 - USE OF NIR AND PLS IN QUALITY CONTROL OF CARBOXYMETHYLCELLULOSE

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Near infrared spectroscopy (NIR) and Partial Least Squares (PLS) have been used to monitor the industrial production of carboxymethylcellulose, in order to predict the most important quality parameters, such as water amount, substitution degree, active content and impurities.
The data set was made by 101 samples, from four different products.
Very good results have been obtained by developing a single model for each response, containing all the products. This simplifies the procedure of quality control and allows to obtain robust models in a short time span.
The prediction ability of the models has been tested on an external test set, created by splitting the original data set according to the production date, with the first 70 samples in the training set and the last 31 samples in the test set. By doing this, also the robustness of the models versus possible time related variations of the industrial process can be tested.
For all the responses the prediction errors on the test set were very satisfying, in many cases not significantly larger than the experimental errors. These results will allow our company to use NIR spectroscopy as a powerful tool in on line process monitoring; beyond the specific case reported in this work, in the future this analytical technique will be applied to all chemicals deriving from natural raw materials.

O30 - NEW TOOLS FOR DATA PRE-TREATMENT IN LC-MS-BASED METABOLOMICS

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Metabolomics based on LC-MS is largely applied to medicine, food chemistry and biological studies. In particular, untargeted LC-MS is often applied to obtain a holistic representation of the system under investigation [1]. Large and complex data sets are produced and suitable tools are needed to extract the hidden information.
Computer-assisted analysis of LC-MS data sets is possible and actually capable of performing most of the routine analyses. Untargeted metabolomics based on LC-MS can benefit from these tools. In this study we show how ACD/IntelliXtract (Advanced Chemistry Development, Inc.) can be used for performing data-pre-treatment in order to obtain raw data componentization and focus the data analysis process on real metabolites. ACD/IntelliXtract is able to remove noise, identify possible neutral losses, evaluate isotope patterns, check 12C/ 13C ratios, determine the molecular weight of different chromatographic components, examine adducts and multimer ions. The alignment of the experiments is discussed and an automatic workflow to produce data sets to submit to statistical data analysis is presented. A case study where two groups of rats (control against treated rats) are compared by analysing urine with HPLC-ESI-MS is discussed.

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O31 - FLUORESCENCE SENSING AND CELLULAR IMAGING OF Cu^{2+} BY A NEW WATER SOLUBLE CHEMOSENSOR

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Metal ions play crucial roles in living systems and have an extremely remarkable eco- and toxicological impact on both environment and humans; consequently the detection and quantitative determination of metal ions has long received considerable attention. Among transition metals, Cu^{2+} carries out key functions as, *inter alia*, a catalytic cofactor for a variety of metalloenzymes. Alteration of the homeostatic levels of Cu^{2+} has been observed both in biological fluids and tissues of patients affected by cancer as well as in some neurodegenerative disorders. The need for molecular systems able to effectively recognize copper ions in solution and work in living organisms has increased in the last years. Chemosensors based on ion-induced changes in the fluorescence response have been proposed as useful detecting agents due to their high sensitivity, selectivity and quick response. However, solubility is a major issue for the successful application of such sensors in biological systems.
In this context, we have derivatized a poorly water soluble sensor, initially proposed by Xu *et al.* [1], with a sugar moiety (trehalose) to obtain a Cu^{2+} chemosensor that maintains the molecular scaffold of the former ligand and may work in the turn-on mode while having a satisfactorily solubility in water. The ability of a chemosensor to bind and detect a metal ion depends on the solvent, temperature and pH. Consequently, an accurate speciation and study of the acid-base features of the ligand is mandatory to figure out the best pH window that allows for a useful application of the sensor. In this work, we report on the synthesis of a water-soluble trehalose-derivatized amine-based chemosensors, its proton and Cu^{2+} complexation properties and its selectivity for Cu^{2+} over other metal ions. Proof-of-working experiments of live cell imaging were also carried out on differentiated neuroblastoma SH-SY5Y cells to demonstrate that the chemosensor can track the presence of Cu^{2+} ions in a cellular environment.

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O32 - BINDING ABILITY OF PHOSPHONIC NTA DERIVATIVES TOWARD BIOLOGICALLY AND ENVIRONMENTALLY RELEVANT METAL AND ORGANOMETAL CATIONS

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The outstanding peculiarities of phosphonates are well known since many time. Nowadays, these ligands are used in a broad variety technological and industrial processes (including, e.g., nanomaterials), and are of great interest also in the environmental, biological and medical fields. Their versatility is mainly due to their chemical stability (also to breakdown by enzymatic hydrolysis), their structural analogies with some natural compounds and, ultimately, to their coordination chemistry. With respect to this last aspect, also the IUPAC affirmed that, "the broad and intensive applications of organophosphonates require reliable data on the stability constants of the corresponding complexes in order to permit equilibrium modeling and prediction of the important technological, environmental, and pharmacokinetic equilibria.", sustaining the preparation of a "critical evaluation of stability constants of phosphonic acids". [1] In this light, in this contribution we report some results on the stability of the aqueous complexes formed by the mono-, di-, tri- phosphonate derivatives of nitrilotriacetic acid (NTA) with Hg^{2+}, CH_3Hg^{+}, Sn^{2+}, and $(CH_2)_2Sn^{2+}$. Due to the above-cited variety of applications these ligands may have, some measurements, including those for the determination of their acid-base properties, have been performed in different ionic media and in the $0 < I$ / mol $L^{-1} \leq 1.0$ ionic strength range, in order to define their speciation in a series of natural fluids and other aqueous solutions coming from various technological processes. The dependence of the stability (and protonation) constants on ionic strength has been modeled by and extended Debye–Hückel equation. Obtained results have also been compared to those related to the "simple" NTA and, where literature data were unavailable or unreliable, like the case of Sn^{2+}, some experimental measurements have been performed for completeness. Finally, the sequestering ability of various ligands toward the investigated cation has also been quantified in various conditions

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O33 - SURFACE CHEMICAL PROPERTIES OF TETRALKYL-AMMONIUM CARBOXYLATES

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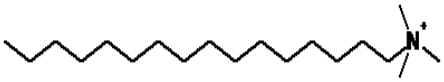
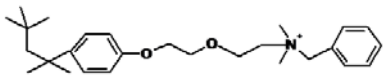
Tetralkylammonium carboxylates are used as detergents, corrosion inhibitors and anti–rust agents in the petrochemical industry. Their use in the development of sensitive potentiometric electrodes to surfactants [1] is also reported. In the present work the surface chemical properties of the benzethonium laurate and the cetyltrimethylammonium laurate, were investigated.



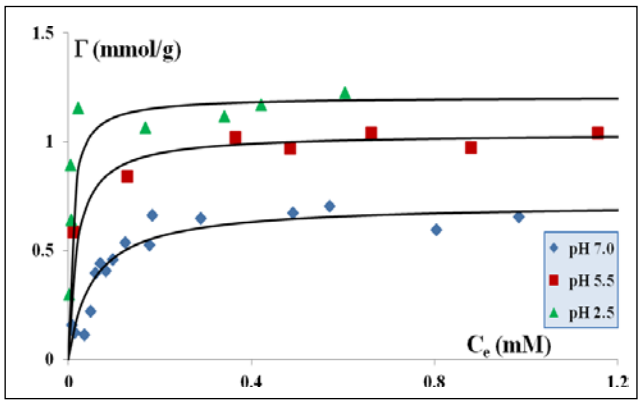
cetyltrimethylammonium ion



benzethonium ion

The adsorbent capacities of Naphthol Yellow S, a dye used in paper, plastics, textile and food industries [2], have been studied. The measurements were carried out at 25° C in suspensions containing NaCl 0.1 M as ionic medium. The surface chemistry properties of the two solids were studied by potentiometric methods, by measuring the surface charge as a function of pH.

The interaction solid–dye was monitored by determining the amount of analyte adsorbed per gram of solid (Γ, mmol/g), as a function of time, until equilibrium was reached. The free concentration of dye (C_e) was determined by spectrophotometry.



The experimental data are in agreement with a kinetic of pseudo second order. The adsorption isotherms were obtained at 25° C in suspensions in NaCl 0.1 M, in the pH range between 2.5 and 7.0. The isotherms can be interpreted according to the Langmuir model.

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O34 - SEQUESTRATION OF Sn^{2+} BY DIFFERENT LIGAND CLASSES IN AQUEOUS SOLUTION

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Tin compounds are divided into two main classes: 1. tin metal and inorganic tin salts, with tin valency of 2+ or 4+; 2. organotin compounds, having general formula R_nSnX_{4-n} (n = 1-4), where R and X are an organic group and an ionic species, respectively. The presence of tin and organotin compounds in the environment is due to numerous uses in a wide range of industries. In the aquatic environment, the chemical form of dissolved tin (Sn^{2+} or Sn^{4+}) depends on the conditions prevailing in the medium. The presence of methylated tin compounds in non-polluted waters is mainly due to bio-methylation by aerobic and anaerobic bacteria.
In literature are present several studies on the aqueous solution chemistry of organotin(IV) compounds [1]. On the contrary, the papers on the speciation of inorganic tin in aqueous solution and in particular on Sn^{2+} are very few. The causes may be mainly attributed to the formation of sparingly soluble species already at acidic pH and at millimolar concentration, the very strong hydrolysis at low pH values (≥ 2) and the strong oxidation. For this reason, in recent years, a systematic study on the interactions of Sn^{2+} in aqueous solution, with particular reference to the hydrolysis and the complex formation with inorganic and organic ligands of biological and environmental interest has been undertaken by this research group [2,3]. The ligand classes studied are carboxylates, amines, amino acids, mercaptocarboxylates. The analytical techniques used are mainly potentiometry and voltammetry and, in some cases, also titration calorimetry. The sequestering ability of the different ligands has been investigated through the speciation studies with the aim to obtain predictive equations having general validity for ligand classes and to build models for natural fluids. Some empirical relationships, useful to predict the stability of species not experimentally determined, has been calculated, as a function of the kind and number of functional groups.

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O35 - MESOPOROUS SILICA DERIVATIZED WITH 1-(3'-AMINOPROPYL)-3-HYDROXY-2-METHYL-4-PYRIDINONE: DEVELOPMENT TRIVALENT METAL IONS SENSORS.

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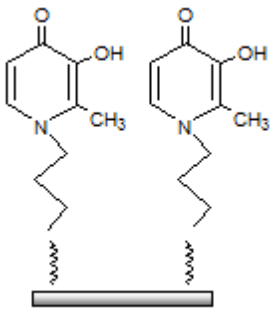

Figure 1- Scheme of the ligand anchored on the solid phase

The hydroxypyridinones are known to be ligands sufficiently stable to be employed in medicine as potential sequestering agents of undesired trivalent metal ions, i.d. Fe(III) and Al(III), or carriers of specific ions such as La(III). In this research we functionalized the mesoporous silica, MCM-41 with a hydroxypyridinone, to obtain a device, represented in Fig 1, for sensing of these ions. Several derivatives of 3-hydroxy-4 pyridinones have been, and still are, under study. We selected the AHP, 1-(3'-aminopropyl)-3-hydroxy-2-methyl-4-pyridinone, carrying an amine as substituent on the nitrogen atom. We fixed it on the MCM-41, previously derivatized with GPTMS. The solid was subjected to elemental analysis: a concentration of active groups equal to 0.48 mmol / g was found. Both IR spectra and TGA experiments showed the successful functionalization of silica. The TEM/SEM analysis on the solid phase loaded with iron(III) showed a homogeneous distribution of the sites, which corresponds to a concentration, referred to iron ion, about 2 mmol / g. The kinetic of Fe(III) and La(III) sorption was found similar to other analogous functionalized silica. In the case of Fe(III), 5 h occurred to reach equilibrium, longer times for LaIII). The nature of the interaction between the metal ion of interest and the AHP-MS was investigated on the basis of sorption and desorption experiments, under controlled conditions. According to our findings, Fe(III) is sorbed, at pH 2.5, with a prevalence of a complex with stoichiometric ratio M:L = 1:2, while it is quite clear that for La(III), a stoichiometry M:L = 1:3 is prevalent, since quantitative sorption occurs at pH around neutrality. Further investigations are going on to fully characterize of metal sorption, but the selectivity towards trivalent metal ions, particularly towards Fe(III), makes AHP-MS a very promising material to test unknowns solutions for their metal content and to get information about metal species distribution, from the faction sorbed on the solid, under given condition. This application, while out of the context of the present study, will be soon investigated.

O36 - METHODOLOGICAL ASPECTS IN THE STUDY OF ALKALI METAL ION WEAK COMPLEXES

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The detection of alkali metal complex formation with polycarboxylate, hydroxo- polycarboxylate and amino-polycarboxylate ligands has been investigated employing ISE-Na^+ potentiometry. The coordination chemistry in solution of alkali metal ions was relatively little investigated [1], in particular if compared with the great number of results reported in the literature for complexes of transition metal ions. Nevertheless, with the aim of correctly solving analytical problems, in building chemical speciation models for interpretation of natural chemical system behavior, the formation of alkali metal complexes cannot be neglected. According to the NEA authors [2], the existence of complexes with alkali metal ions "should not be considered as completely proven" by measurements carried out at different ionic strengths, because the results depend on the model used for activity coefficients. In this work, to minimize the effects due to the variation of activity coefficients, a set of measurements were made at constant ionic strength. The formation of alkali metal complexes in solution has been evidenced unequivocally comparing the experimental values of free Na^+ ions with those of total sodium added for each point of titration curve. There are no doubts about the formation of alkali metal complexes in solution. After detection, the formation constants were determined and their values show a good agreement with those evaluated by pH-metric technique or by ISE-Na^+ potentiometry at variable ionic strengths, suggesting that also potentiometric techniques at variable ionic strengths can be used in the study of this topic with a good accuracy. Moreover, our results confirm the low stability of alkali metal complexes in aqueous solution, which is founded on coulomb interactions. In general, the values of stability constants depend not only on the number of charged oxygen donor groups, but also on the presence of amino donor(s) and hydroxyl groups.

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O37 - MICRORNAS DETECTION IN A DROPLET MICROFLUIDIC DEVICE

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An accurate detection of microRNAs (miRNAs), small noncoding RNA molecules, has emerged as an important procedure for the early diagnosis of important diseases. MiRNAsare involved in almost every biological process, including cell fate determination, proliferation, and cell death [1].Droplet-based microfluidics defines new and very powerful approaches for biomolecular diagnostics as a consequence of the capability to miniaturize standard laboratory operations using nano/femto-liter volume of reagents in significantly less time [2]. Each droplet can be considered as an isolated microreactor which can be individually controlled and analyzed. This allows parallel processing, higher throughput and less sample consumption than continuous flow systems. Recently we used droplet-based microfluidics and peptide nucleic acid molecular beacons for the detection ofpolymerase chain reaction (PCR)-amplified DNA sequenceswithin nanoliter-sized droplets [3].In this communication the combined use of a droplet-based microfluidic system and a circular strand displacement isothermal amplification method is described for the selective detection of microRNA in nanoliter droplets. The method exploitsmolecular beacon (MB) structures in order to detect fluorescence changes occurring during probe-target hybridization reactions. In particular, we focused our research work on miR210, a robust target of hypoxia-inducible factor [4]. Compared to standard PCR-based amplification methods isothermal amplification methods not requiring any thermal cycling are easier to operate and make simpler their integration in microfluidic devices. The nanomolar sensitivity and specificity provided by the described detection method, together with the nanoliter volumes of droplets used in this analytical approach, allow an easier, simpler and more accurate detection of miR210 than standard methods today available.

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O38 - SURFACE CHARACTERIZATION OF NOVEL ANTIBACTERIAL ANODIC SPARK DEPOSITION TREATMENTS FOR TITANIUM SUBSTRATES

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Titanium and titanium alloys represent the biomaterials of choice in applications involving hard tissue replacement, especially for dental and orthopaedic fields. Surface modifications are required to improve implants lifetime increasing their clinical performance. Orthopaedic and orthodontic infections represent one of the major causes of implant failure [1]. An interesting strategy to overcome this problem consists in developing new biomimetic treatments for Ti characterized by antibacterial properties. In order to achieve this goal, surface treatments using the anodic spark deposition (ASD) have been proposed. This electrochemical technique allows to obtain homogeneous titanium oxide surfaces characterized by microporous and nanorough topography with a modified surface chemical composition enriched by the elements present in the electrolytic solution. Four different silver or gallium-based ASD surface treatments, called AgCis, AgNPs, GaCis and GaOss, were developed on Ti samples. Untreated Ti and a previously developed osteointegrative ASD coating, called SiB-Na, were used as controls [2]. The samples characterization was performed by SEM/EDX and XPS analyses, while silver or gallium release was investigated using ICP/OES. Important features were achieved by XPS: in particular, analyzing the Ti2p signals, additional contributions ascribed to titanates of different heteroatoms (Si, Ca, Na, P) can be observed. The presence of titanates on the surface could positively influence the mineralization process and the osteoblast proliferation and differentiation [3]. Moreover, the oxidation states and the surface amount of the different antibacterial elements (Ag or Ga), obtained by XPS, have been correlated to substrate antibacterial properties. Indeed, antimicrobial characterization, performed by *S.epidermidis, S.mutans* and *E.coli*, evidencing a strong long-lasting antibacterial activity against all the bacteria strains.

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O39 - ANALYTICAL CHARACTERIZATION OF HYBRID COPPER-CHITOSAN NANOANTIMICROBIALS SYNTHETIZED BY FEMTOSECOND LASER-ABLATION IN LIQUID

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Copper-chitosan (Cu-CS) nanoantimicrobials are a novel class of bioactive nanosized agents providing enhanced/synergistic efficiency in the prevention of biocontamination in several application fields. [1] In fact, copper nanoparticles embedded in water insoluble polymers may provide an exceptionally controlled ionic release when exposed to aqueous media, thus inhibiting microorganism growth without being toxic for humans. [2]
In the present study, the Laser Ablation Technique has been operated in the femtosecond regime to synthesize Cu-CS antimicrobial nanomaterials, combining the bioactivity of both components. The influence of experimental parameters, including the CS concentration in the ablation media has been systematically assessed. As a result, Cu-CS composite colloids at different Cu/CS molar ratios have been prepared in aqueous media.
Cu-CS nanocolloids have been used as such, or mixed to a third bioactive material, such as Eudragit®. Hybrid solutions have been eventually deposited as thin films on different substrates.
Nanocolloids and nanostructured coatings have been extensively characterized by several spectroscopies, including UV-Vis, Fourier Transform InfraRed and X-ray Photoelectron Spectroscopy. The nanoparticle morphology has been evaluated by Dynamic Light Scattering and Transmission Electron Microscopy. Bioactivity tests have been performed on several target microorganisms, as well.

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O40 - USE OF 1,8-BIS(DIMETHYL-AMINO)NAPHTHALENE/9-AMINOACRIDINE AS A NEW BINARY MATRIX FOR PROFILING OF WHOLE CELL BACTERIA BY MATRIX ASSISTED LASER DESORPTION IONIZATION MASS SPECTROMETRY

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Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS is increasingly used for lipid analysis due to its high sensitivity (required amounts in the order of a few pmol), high throughput and tolerance towards salts eventually present in crude sample extracts[1]. Nevertheless, relatively low molecular weight (LMW) analytes, such as most lipids, require some special properties of the MALDI matrix[3]. The use of a DMAN matrix for direct MALDI-TOF MS analysis of lipidome in intact Gram positive bacterial cells (*Lactobacillus sanfranciscensis and plantarum*) has been recently demonstrated in our laboratory[3].
In the present work, the effectiveness of a novel binary matrix composed of two strong bases *i.e.* 1,8-bis(dimethyl-amino)naphthalene (DMAN; proton sponge) and 9-aminoacridine (9AA) for the lipidomic characterization of whole bacterial cells by matrix assisted laser desorption ionization mass spectrometry (MALDI MS) is presented. The behaviour of matrices was deeply investigated by means of different spectroscopic techniques including X-Ray Photoelectron Spectroscopy (XPS) and some mechanisms in proton trasfer performance are razionalized.
Deprotonated analyte signals nearly free of matrix-related ions were observed in negative ion mode. The main critical experimental parameters effect (laser energy, pulse voltage, DMAN/9AA ratio, analyte/matrix ratio) was investigated. XPS was employed to explore the chemical surface composition of single or mixed matrices and XPS imaging experiments were runned to map the spatial distribution of a model phospholipid.
The DMAN/9AA binary matrix was then successfully applied to the analysis of both intact Gram positive or Gram Negative microorganisms.

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O41 - MEASUREMENT OF ISOTOPIC COMPOSITION OF ATMOSPHERIC LEAD IN POLAR REGIONS BY REACTION CELL INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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The lead isotopic composition of aerosols reaching the polar regions potentially contains valuable information about sources and long-range transportation of atmospheric particulate and associated contaminants, proving to be an useful complement for meteorological and elemental composition studies 00. In the frame of the Italian polar research programmes, samples of atmospheric aerosols have been systematically collected in both Norwegian Arctic (Ny-Ålesund, Svalbard Islands) and Antarctica (Terra Nova Bay, Victoria Land) and analysed for elemental composition and stable lead isotope ratios ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$).
Accurate and precise determination of lead isotope ratios in digests of particulate samples has been obtained by inductively coupled plasma mass spectrometry (ICP-MS), using the dynamic reaction cell to improve the precision 0. The relevant operating parameters have been optimized in a multivariate way, according to the empirical modeling and experimental design concepts. This allowed the full consideration of mutual interactions among the factors as well as the minimization of %RSD-values and mass discrimination effects.
After determining the detector dead time, the following instrumental parameters have been studied: settling time, the rod offset voltages of both the quadrupole and the reaction cell, the Mathieu stability parameters of the cell's quadrupole, the cell path and the axial field voltages, dwell time and number of sweeps. Moreover, the use of argon, methane and ammonia as the collision gas was explored and the measured isotope ratio precision compared to that attainable with standard quadrupole-based ICP-MS and theoretical values.
The main figures of merit of the optimized method have been determined according to the IUPAC recommendations, with special attention to the robustness and the limit of quantification at a given precision threshold.
The results of the method optimization and validation and some preliminary data for the analysis of particulate samples will be reported and discussed.

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O42 - DEVELOPMENT AND CHARACTERIZATION OF ACTIVE ANTIMICROBIAL PACKAGING OBTAINED BY SOL-GEL TECHNIQUE

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Packaging plays many important roles in the food supply chain to ensure safe distribution and storage of products. Usually, classical packages offer only passive protective function, whereas, active food packaging is usually referred to a packaging system that interacts dynamically with the product it contains and/or the surrounding environment, which results in the activation of some mechanisms to extend the shelf-life or quality of the product. On other hand, today this concept is of special importance in the area of fresh and extended shelf life foods. The antimicrobial active packaging is a technology that inhibits or retards the proliferation of microorganisms in foods, thus extending the shelf life of the product. The application of antimicrobial films allows the migration of the antimicrobial to the coating surface and provides a continuous antimicrobial effect on the food during extended exposure. In this type of packagings an antimicrobial agent can be incorporated into polymers, as well as coated or adsorbed onto polymer surfaces. The use of polymers as carriers of antimicrobials not only permits controlled release of these antimicrobials but also prevents dramatic reductions in their activity due to their affinity for food particles and inactivation by components in foods.
Recently, we demonstrated that active antimicrobial packagings can be obtained by incorporating as antimicrobial agent lysozyme into poly(ethylene terephthalate) (PET) substrates. The aim of this study was the development of an antimicrobial coating, obtained by sol-gel technique, in which natamycin was physically entrapped in the network of thin coatings.
The films were obtained by dip coating process, using plasma activated poly lactic acid (PLA) as substrate. The effect of organic-inorganic ratio on the natamycin release was evaluated. Effectiveness of the natamycin released from PLA-based films was performed by capillary electrophoresis-mass spectrometry (CE-MS), and by HPLC coupled with UV-DAD-detection.
The migration of antifungal into food simulating liquid (FSL, water and ethanol 50:50, v/v) was experimentally measured and mathematically modelled. The antifungal properties of the films were investigated on the surface of commercial semi-soft cheese. Results are presented and discussed.

O43 - CHEMILUMINESCENCE-BASED BIOSENSOR FOR FUMONISINS AND AFLATOXINS QUANTITATIVE DETECTION IN MAIZE SAMPLES

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Aflatoxins and fumonisins, two mycotoxins mainly found in corn and derived products, are known for their acute toxic, immunosuppressive, mutagenic or even carcinogenic effects. Several instrumental analytical methods are currently available for detecting these toxins in foodstuff, but they require complex sample preparation and dedicated laboratory equipment.
Biosensors are very promising analytical tools for rapid on-site detection of analytes in complex matrices. We recently described a biosensor for type-B fumonisins detection in maize samples based on a chemiluminescence Lateral Flow ImmunoAssay (CL-LFIA) coupled with a portable ultrasensitive CCD-based "contact" imaging device, reaching a limit of detection of 25 μg kg^{-1} in maize flour samples [1].
In this work, a multiplex CL-LFIA is presented, in which two competitive immunoassays are simultaneously performed on the same strip for detecting type-B fumonisins and B1 aflatoxin. The assay involved a simple extraction of the analytes from maize flour samples followed by their detection by a multiplex competitive immunoassay with chemiluminescent (CL) detection employing ready-to-use analytical cartridges. The use of CL detection allowed accurate and objective analytes quantification, down to picomoles, rather than qualitative or semi-quantitative information usually obtained employing conventional LFIAs based on colloidal gold labelling. In the future, the portable device will enable the analysis directly on field and, by simultaneously detecting several mycotoxins in one sample, provide multiple information through a single analysis.

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O44 - OPTIMIZATION OF THE EXTRACTION OF THE VOLATILE FRACTION FROM HONEY SAMPLES BY SPME-GC-MS, EXPERIMENTAL DESIGN AND MULTIVARIATE TARGET FUNCTIONS BASED ON PRINCIPAL COMPONENT ANALYSIS

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In the last years increasing attention has been devoted to the characterization of the profile of volatile molecules in honey samples above all in authenticity and adulteration studies, since the commercial value of honey is usually strictly correlated to its botanical and/or geographical origin. The volatile profile is usually determined by Head-Space Solid Phase Micro-Extraction (HS-SPME), followed by GC-MS.
When HS-SPME is used, particular attention has to be paid to the optimization of the extraction procedure that is subjected to the effect of several experimental parameters, as conditioning time, extraction time and temperature, ionic strength, amount of sample, water:sample ratio, sample solution:headspace volume ratio and type of fiber used for SPME.
Moreover, one of the drawbacks of SPME is its low repeatability, if compared to other extraction techniques. Usually, optimization in SPME is carried out to maximize sensitivity, i.e. gas-chromatographic peak areas, while maximization of repeatability is usually neglected. Another point that is usually not addressed to is the accomplishment of a real multivariate optimization: the best experimental conditions are in general achieved for a set of selected analytes independently, usually belonging to different chemical classes to provide general conditions for the compounds most representative of the classes of analytes present.
To overcome these limitations, optimization of both sensitivity (chromatographic peak areas) and repeatability (variation of each peak area across replications of the same experiment) was carried out here by the use of experimental design techniques. Three factors underwent optimization: temperature and time of extraction and the ionic strength (amount of salt added). Each experiment was evaluated by a multivariate target function that allows to take into consideration all the analytes at the same time while preserving the information about their different characteristics, reflecting in their different elution time: Principal Component Analysis (PCA) was used as dimensionality reduction tool, to provide a multivariate target function during the optimization phase taking into account all the analytes, each one described by its own area (for sensitivity optimization) or coefficient of variation (for repeatability optimization). Optimal extraction conditions were identified for both sensitivity and repeatability and a final global compromise was also reached.

O45 - TERROIR DIFFERENTIATION OF LAMBRUSCO PDO WINES BY STRONTIUM ISOTOPIC SIGNATURE

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The interest of consumers, as well as of producers, toward origin and quality of food has increased over the last years. As regards the oenological field, the quality of wine is in many cases related to the concept of *terroir* (history, geographical origin, typical raw materials and methods, ecc.). In this context, the assessment of the link between the territory of origin and the food product by means of analytical indicators represents a challenging target, useful for the valorization of the product itself. Among the different indicators used for geographical traceability studies, the $^{87}Sr/^{86}Sr$ isotopic ratio (Sr-I.R.), has provided excellent results for different types of food.
The present research is part of a project dealing with the development of authenticity and geographical traceability models of PDO Italian wines [1], with particular reference on *Lambrusco* wines, which are one of the main typical products of the Modena district. The possibility of obtaining reliable traceability models is mainly linked to the capability of monitoring the considered indicator in a representative set of investigated matrices: mainly soil and wines. Thanks to the collaboration with Consorzio Marchio Storico dei Lambruschi Modenesi, it has been possible to measure the Sr-I.R. on a statistically representative set of *Lambrusco* wines, commercially available and produced in 2010, 2011 and 2012. Furthermore, Sr-I.R. values of wines were compared with the Sr-isotopic ranges of Modena soils, with the aim to verify and establish a link with the respective territory of origin. The selection of representative, informative and different soil samples of the Modena district was accomplished in a previous work by means of Design of Experiment techniques, in order to ensure a sustainable and rational mapping of the investigated geographical area, taking into account properties related to geological features and production variables (grape varietals and produced quantities) [2]. Finally, the Sr-I.R. was also determined on vine branches, collected in proximity of each soil sampling point, since previous researches highlighted an improvement of the correlation with food and a better discriminating power, when considering branches instead of soil [3].

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O46 - CHARACTERIZATION OF THE UNSAPONIFIABLE FRACTION OF OLIVE OIL FROM UNRIPED FRUITS AND ITS APPLICATION IN THE TREATMENT OF RHEUMATOID ARTHRITIS

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Aim of the work was to explore the efficacy of the unsaponifiable fraction (UF) of olive oil from *Oleaeuropaea*unriped fruits in the topical treatment of rheumatoid arthritis (RA), a systemic inflammatory disorder.In particular we have: i) investigated by GC-MS analysis which maturation stage of the fruits (cultivar Gentile di Chieti) could give the maximal yield in anti-inflammatory structures; ii) once identified the maximal yield period, isolated the unsaponifiable fraction (UF) from the olive oil obtained by conventional methods; iii) carried out a preliminary evaluation of its efficacy in the topical treatment of RA, with an UF-containing ointment.The UF of olive samples (5 gr), harvested weekly from the 20th until the 32th week after flowering, was obtained as reported in literature. The yield of the UF at the 22th week was nearly 5 times greater (2.46%) than that of the 32th week (0.5%). Each of the anti-inflammatory UF components was analyzed by GC-MS, and identified by its RT and MS behavior (NIST library 2.0). The quali-quantitative analytical profile of the UF at the 22th week was: squalene (30%), α-tocopherol acetate (12,23%), α/β-amyrins (18%), β-sitosterol (15%), lanosterol (4,5%), stigmasterol (3,2%) and other minor cyclic phytosterols (13%).The concentration of the anti-inflammatory constituents progressively decreases subsequently, in parallel to the drop of the UF yield.Hence the UF of the olive oil from the 22th week was employed to prepare an ointment containing shea butter, bees wax, olive oil, UF (5%) and essential oils.10 human volunteers (mean age 60.2 yr) affected by moderate RA, recalcitrant to conventional pharmacotherapy, were enrolled in the study and instructed to the contralateral self-application (3 times/daily, 4 weeks) on the inflamed joints of knees and hands, of the ointment and of the vehicle. The efficacy of UF treatment was evaluated weekly by the physician considering the typical signs of RA: swelling, redness, pain sensation, heat, and loss of motility. For all the parameters a significant improvement was observed with a complete disappearance of the signs of the inflammation at the end of the treatment (the score was reduced from 4, worst, to 0, best). No skin reaction was observed.The results of this preliminary study suggest the strong potentiality of the UF from the oil of unriped fruits in the topical treatment of this inflammatory disease.

O47 - GLUCOSINOLATES AND ACYL CONJUGATES DIVERSITY IN *B. vulgaris* SEEDS EVALUATED BY LC/MS USING FOURIER-TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY AND INFRARED MULTIPHOTON DISSOCIATION (FTICR-MS IRMPD)

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Glucosinolates (GSLs) are nitrogen- and sulfur-containing metabolites that contribute to human health and plant defense. Around 130 individual GSLs have so far been reported, and the number of documented structures is steadily increasing [1]. The majority of the currently known diversity is due to differences in the amino acid derived part of the GSL molecule [2]. However, another type of diversity arises from conjugation of GSLs with naturally occurring carboxylic acids (e.g., isoferulic acid), giving rise to so-termed acylated-GSLs. Indeed, of the newly documented GSLs in the last decade, the majority were acylated ones [3]. In this communication, the LC profiling of intact GLSs and acylated-GLSs in *B. vulgaris* seeds by using electrospray ionization (ESI) and Fourier-transform ion cyclotron resonance (FTICR) mass spectrometry (MS) is presented. Structural information was obtained upon precursor ions' isolation $[M-H]^-$ within the high resolution trapping cell and subsequent fragmentation induced by infrared multiphoton dissociation (IRMPD). All compounds, as deprotonated species, were identified by accurate m/z values (mass errors lower than +0.75 ppm) and IRMPD fragmentation of precursor ions. In the IRMPD mass spectra, several common ions, diagnostically useful for establishing their membership in the general family of GLSs, and product ions, useful for side chain identification, were observed. Along with most common GLSs and acylated-GLSs already found in *B. vulgaris* seeds such as glucobarbarin, glucoarabihirsuin, glucobrassicin, gluconasturtiin, 6'-isoferuloyl-glucobarbarin, 6'-isoferuloyl-glucobrassicin and 6'-isoferuloyl-gluconasturtiin, the occurrence of the uncommon 6'-coumaroyl-glucobarbarin, 6'-sinapoyl-glucobarbarin and 6'-dimethoxycinnamoyl-glucobarbarin is reported. Besides, the presence of eight already known GLSs was found in some accessions. It was confirmed that the profiles of isoferuloyl derivatives matched the profiles of non-acylated GSLs.

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O48 - EMERGING POLLUTANTS IN RIVER WATER: NON-TARGET ANALYTICAL DETERMINATION OF THEIR TRANSFORMATION PRODUCTS

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Emerging pollutants (EP) determination, even if is not a new issue, is recently become a priority concern and a growing interest arose toward the screening for identify non-target compounds in environmental samples, including metabolites and degradation products.
A major class of EP comprises pharmaceuticals; in particular, antibiotic and anticancer drugswere identified as an important topic as, at present, the first ones are among major sources of bioactive molecules in water and, the second onesneed to be overlooked owing to their cytotoxicity, genotoxicity, mutagenicity and teratogenicity.Another class of EP of increasing awareness is nanomaterials.With this in mind, this study was aimed to enlighten the fate of selected EPsin Po river water: two widely diffused antibiotics, lincomycin and clarithromycin, an antiepileptic drug, carbamazepine, two anticancer drugs, cyclofosfamide and methotrexate and a nanomaterial, fullerene, were investigated. We focused on the EPs degradation and identification of their transformation products, aimed to recognize their main transformation routes following their discharge in the environment. Analyses were performed by liquid chromatography-LTQ-FT-Orbitrap mass spectrometryusing an Electrospray Ionization (ESI) interface, a powerful analytical tool for the analysis of these contaminants in environmental matrices.
Initially, laboratory experiments were performed on river water spiked with EPs to simulate all possible transformation processes occurring in the aquatic system. Then, all the possible main and secondary transformation products (TPs) were searched for in samples collected from the Po River. The selected EPs and several TPs were detected in all samples. This approach permitted not only to assess the selected EPs presence in natural waters, but also to identify which of the transformation routes recognized in simulation experiments also occurred in the aquatic environment. Specifically for the case of carbamazepine, it was possible to find some key TPs that could be considered as markers for its photochemical environmental transformation in the aquatic environment.

O49 - ARCTIC AEROSOL MEASUREMENTS: SAMPLING STRATEGIES AND FIRST RESULTS.

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The Arctic is the world region most affected by the present global warming, since the climate forcing is causing dramatic environmental changes in a complex cycle of feedback processes. In particular, the Arctic is undergoing relevant variations of marine and coastal eco-systems, including large changes in extension and thickness of the annual and permanent sea ice and in the permafrost superficial structure. Besides, changes in temperature profiles along the uppermost seawater layers and in the troposphere air column could involve relevant variations of the marine and atmospheric circulation processes, able to significantly amplify the climate forcing on a hemispheric scale. Arctic aerosol is believed to play a relevant role in these climate-environment feedbacks by scattering and absorption processes of the solar radiation and by promoting the cloud formation, so affecting the superficial albedo and the hydrological cycle. Although these effects are well known, large uncertainties affect not only their quantitative evaluation, but also the sign of the variation. In order to improve our knowledge on the Arctic aerosol, two sampling and direct measurements campaigns were carried since 2010 at Ny Alesund (78.6 °N, 11.6 °E), Svalbard Islands, from March to September. Direct observations included absorption (black carbon) and nephelometric (aerosol optical properties) measurements, as well as high-resolved and high-frequency aerosol particle sizing. Size measurements were carried out by an integrated system (TSI SMPS and TSI-APS) able to give a 106-size-classes spectrum, ranging from 10 nm to 10 um, every 10 minutes. Size-segregated aerosol was collected by several sampling systems: two PM10 low-volume samplers (aerosol was collected on Teflon filters for inorganic components and on quartz filters for EC-OC measurements), two multi-stage impactors (4-stage (>10, 10-2.5, 2.5-1, < 1 um) and 12-stage (> 10 um to 0.040 um), for ions, principal metals and elements analysis), and a medium-volume PM10 collector (for trace metals content). Here, we will show the most relevant results obtained by the on-site measurements of the optical and physical (size) aerosol properties and by the chemical analysis of the PM10 and multi-stage aerosol samples.

O50 - INTEGRATION OF DIFFERENT MASS SPECTROMETRY TECHNIQUES TO STUDY BIOGENIC SECONDARY ORGANIC AEROSOL FORMATION

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Secondary organic aerosol (SOA) formed by oxidation of biogenic volatile organic compounds (BVOCs) accounts for a large fraction of global atmospheric aerosol. Despite significant efforts in elucidating SOA composition and formation pathways, large areas of uncertainty still remain. With respect to these, oligomeric compound formation and its bearing on the unaccounted fraction of organic aerosol needs further investigation.
In the present study, secondary organic aerosol was produced in a new 5 m^3 Teflon film smog chamber located at the Department of Chemistry of the University of Cambridge (UK). α-pinene and BVOC mixture (α,β-pinene, Δ-3-carene and isoprene) ozonolysis experiments have been performed in dark conditions at different precursor concentrations. Gas phase oxidation products have been analysed on-line by a proton transfer reaction mass spectrometer (PTR-MS) which allows real-time measurements of most volatile organic compounds with high sensitivity, high time resolution and low ionisation-induced fragmentation [1]. SOA formation has been followed on-line with a scanning mobility particle sizer (SMPS) and extractive electrospray ionisation mass spectrometry (EESI-MS). EESI is a novel ionisation technique developed in-house for the molecular characterisation of organic aerosol with high time resolution [2]. Characterisation of SOA at molecular level has been also performed off-line by sampling on filters followed by solvent extraction and analysis with direct infusion nanoelectrospray ionisation ultrahigh resolution mass spectrometry [3]. Particular attention has been devoted to formation of high molecular weight compounds, which could be produced by oligomerisation of low and semi-volatile first generation oxidation products.

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O51 - DEVELOPMENT OF AN ANALYTICAL APPROACH FOR THE IDENTIFICATION OF FRESHWATER CYANOTOXINS BY USING A LIQUID CHROMATOGRAPHY-QTOF SYSTEM

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A comprehensive risk management related to human exposure to cyanotoxins is limited by feasible analytical tools for monitoring non target algal metabolites. Two analytical approaches based on a liquid chromatography(LC)-Quadrupole-Time of Flight (QTOF) system for the trace determination of freshwater cyanotoxins with and without standards is here presented. A database with more than 150 compounds belonging to several classes of cyanobacteria metabolites, mainly microcystins, has been implemented for the target and non target analysis. The database has been used for a post-run data analysis according a two-steps protocol involving a) the identification of suspect cyanotoxins from their respective accurate (<30 ppm) molecular ions and b) the confirmation of the compound structure via high resolution mass spectrometric (MS) fragmentation in full scan mode.
Alternatively, an automatic MSMS scan using the developed database as a preference list of precursor ions, can ensure all MS structural information in a single chromatographic run. Twenty four extract of surface waters and drinking waters contaminated by cyanobacteria have been processed. These methods allowed the confirmation of target cyanotoxins by comparison with the certified standards, as well as non target detection and characterization of five uncommon variants of microcystins and four anabaenopeptins, two of them as isobaric compounds, fully separated by the LC system.
These different approaches could be used by environmental and health agencies for analyzing cyanotoxins not yet regulated in all matrices, i.e. water, air, food and biological samples, that could be contaminated by cyanobacteria.

O52 - ADVANCES IN TD/GC-MS UNTARGETED COMPOUND ANALYSIS ON PARTICULATE MATTER BEYOND PAHS ROUTINE MONITORING

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The monitoring of some micro-pollutants is routinary because of their potential toxic activity and of normative regulation, but focusing only on some targeted compounds can divert analysts and researchers from identifying pollution macro-events associated to untargeted compounds. Routine analysis of micro-pollutants, as PAHs, in fast scan GC-MS produces Single Ion Monitoring (SIM) chromatograms used for quantitative determination of target compounds but also a Total Ion Current (TIC) signal which can potentially contain interesting unrevealed information. This is specially true when thermal desorption from solid samples as air particulate matter filters is used as pretreatment method; TD/GC-MS transfers analytes to the separation column without discarding some/part of the compounds.
The aim of this study is to report the setup of an experimental and data analysis procedure adequate for disclosing interesting data from raw GC-MS data collections acquired during routine monitoring.
In this communication we present a 3 month daily PAHs routine monitoring near an incinerator in a Friuli Venezia Giulia chair production district in which we collected 120 samples of PM_{10} by quartz filter sampling accordingly to EN12341. A series of raw data (retention time, peak area, peak height, peak width, MW, CAS number) were acquired directly from the data analysis software (meanwhile quantifying PAHs) using the "autointegration" and "MS library search" functions. These data were handled within R free statistical computing environment (http://cran.r-project.org), using a home-made script to filter and intercomparing chromatograms by peak properties. In this way we were able, starting from over 5000 peaks to discriminate, beyond PAHs, 21 relevant peaks present in a great number of samples. Using MS library search reports we were able to identify three molecules with high correspondence to the MS database, which can be related to activities in the sampling site: a plasticizer, a phtalate and an erbicide. These compounds were quantified using corresponding commercial standards.

O53 - UHPLC-TOF MS/MS DEGRADATION STUDIES OF TRICYCLAZOLE FUNGICIDE

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The more recent pesticide formulations are designed to offer advantages of the highest selectivity together with the lowest persistence in the environment. But lower persistence in the environment does not necessarily correspond to lower toxicity, since many pesticides undergo natural degradation reactions that do not lead to mineralization but to the formation of new species potentially more toxic and stable than their precursors [1-3].
This study investigates about the possible degradation reactions undergone in water by tricyclazole, the active principle of "Beam 12", a fungicide formulation largely used in rice cultivation.
The effect of sunlight irradiation and hydrolysis processes was studied for aqueous solutions of the standard tricyclazole and of the commercial formulation through LC-TOF analysis by using a UHPLC system interfaced with a triple TOF mass spectrometer. A new UHPLC-MS/MS method was developed to study the kinetics of the degradation processes and to identify the degradation products. In particular, the software tool IDA (Information Dependent Acquisition) was used to obtain information about the high resolution TOF-MS and TOF-MS/MS spectra.
LC-MS analysis of both tricyclazole and "Beam 12" water solutions undergone to hydrolysis does not evidence new chromatographic peaks with respect to the untreated solutions. On the contrary, LC-MS analysis of the same samples undergone to sunlight irradiation shows a decreased intensity of tricyclazole signal and the presence of new chromatographic peaks. The pattern is similar for the solution of the standard fungicide and of the "Beam 12" formulation. With the help of the high resolution analysis, the chemical structures of the predominant degradation products are proposed.

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O54 - THE ROLE OF MASS FRACTIONATION PROCESSES IN Hg ISOTOPE RATIOS MEASUREMENTS

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Among the global pollutants, Mercury could be considered one of most harmful. For this reason, the study of the distribution and of the sources of this element is relevant for the aims of environmental protection and the human health safeguard. In these contexts, the determination of mercury stable isotopes ratios and, in particular, the identification and the study of fractionation processes seems to be an extremely interesting and challenging field of investigation to verify the "provenance" of the element. Mercury, in fact, undergoes to both mass dependant, MDF, and mass independent fractionation, MIF, processes. In particular the MIF, involving only the odd isotopes (^{199}Hg and ^{201}Hg), appears to be a characteristic fingerprint of the process and the pathways involved in the Hg transformations [1]. Thus, the study of both fractionation phenomena can be a powerful tool to identify its natural or anthropogenic source. In order to have the required precision, the determination of the Hg isotope ratios is commonly conducted by means of HR-MC-ICP/MS instruments. The low magnitude of the MDF and MIF makes the correction of the instrumental mass-bias (MB) a critical step in the determination chain. The most common method for the MB correction assumes an exponential fractionation law and uses for the normalization the Tl isotope ratio [2]. The use of a different element for the MB correction could introduce some errors in the correction step, due to different factors such as the high difference in mass between the normalization couple and the corrected ratio (^{205}Tl/^{203}Tl for ^{199}Hg/^{198}Hg) and differences in the MB factors of the two elements. In order to minimize the possible errors in the correction step, for the Hg some authors report different applications of the exponential law to the MB problem [3]. The evaluation of the influence of the different methods on the data was conducted applying them on the same dataset and comparing the results with the values reported in literature. The dataset was composed by standards (NIST SRM3133) acquired in different session of measurement and coming from the bracketing sequences. Moreover, the influence of the sample matrix and sample preparation technique on the fractionation processes was also investigated acquiring the Hg ratios of muscle samples spiked with the SRM3133 at different concentration.

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O55 - A NEW CLASS OF ANTIOXIDANT COMPOUNDS IN VIRGIN OLIVE OIL: N-O SUBSTITUTED PHENYLALANINE N-HYDROXY

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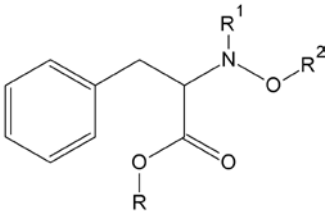
Virgin olive oil (VOO) is unique among the vegetable oils because it is obtained from the olive fruit (*Olea Europea* L.) by solely mechanical means, and thus contains many polar compounds usually eliminated during other treatments. It represents an essential component of the Mediterranean diet and it is considered a healthy food, not only for its fatty acid composition, but also for the presence of minor components having a high biological activity. Among these, phenolic acids, secoiridoids and flavonoids have been widely studied.
Recently, we optimized the extraction protocol of phenolic compounds from VOO, followed by ultraHPLC - electrospray ionization - tandem mass spectrometry (UHPLC/ESI-MS/MS) analysis, using a quadrupole-time of flight (Q-TOF) analyzer. In a liquid-liquid methanolic extract analyzed in positive ESI, we observed a series of intense ion signals with an even *m/z* ratio, and therefore suspected to contain an odd number of nitrogen atoms. This kind of compounds have not been previously reported in the literature. From the accurate *m/z* values of the precursor ions, and the recurring fragments and neutral losses, we inferred that some of them belong to the class of substituted phenylalanine and phenylalanine methyl esters, N-hydroxy, with the general formula:



where R is H or CH_3, R^2 is H, and R^1 is H or a carbonyl (formyl, keto- or carboxyalkyl) group.
Some other compounds are N-O substituted, with R^2 = methyl, tyrosyl, hydroxytyrosyl or dihydroxytyrosyl group.
In addition, few corresponding oximes were also identified.
The accurate masses did not differ from the calculated ones more than 2 ppm. The accurate *m/z* values of product ions also permitted their unequivocal identification, although the low collision energy used with the Q-TOF instrument gave in some cases limited structural information. The sample was also analyzed with a linear ion trap-Orbitrap instrument to obtain confirmatory identification and complementary structural information.
The identification of a new class of compounds solely by high-resolution MS and MS/MS have to be considered only tentative. Attempts are being made to synthesize some of these compounds for a better characterization.

O56 - ULTRA-HIGH PRESSURE LIQUID CHROMATOGRAPHY-TANDEM HIGH RESOLUTION MASS SPECTROMETRY FOR TARGETED AND UNTARGETED ANALYSIS OF POTENTIAL MIGRANTS FROM POLYCARBONATE FOOD-CONTACT PLASTICS

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Ultra-high pressure liquid chromatography (UHPLC) coupled to hybrid mass spectrometry is one of the most selective and sensitive techniques for identification and quantification of organic contaminants and residues in food. More recently, a new line of high-performance benchtop quadrupole orbitrap mass spectrometer has been produced, offering new perspectives in the field of proteomics, metabolomics and analysis of complex matrices [1].
In our work, the ultra-high performance liquid chromatography coupled to quadrupole orbitrap mass spectrometer has been proposed for the use of high resolution to characterize food contact materials. Food contact material includes packaging and any equipment which comes into contact with food. Additives such as UV absorbers, antioxidants and processing stabilizers are often included in plastic composition with the aim of protecting the polymer from its degradation. Moreover, the degradation of such materials, as in the case of polymers, can be responsible for the genesis of new molecules (non-intentionally added substances, NIAS) such as reaction or degradation products, oligomers, impurities. Establishing techniques to detect and quantify any possible migrating compounds, even at low concentrations, is essential to ensure the safe use of any food contact materials.
In this work, the development, optimization and application of a sensitive UHPLC-MS/MS method for the determination of any possible degradation product and additives used in polycarbonate-food contact material will be presented. After optimization of the extraction procedure, two different approaches were adopted. Firstly, targeted analysis was carried out by monitoring several known compounds commonly used as additives, employing data-dependent acquisition with inclusion list. Then, untargeted analysis was also conducted in order to identify unknown molecules such as bisphenol A-degradation products and organic dyes used in polycarbonate food-contact materials.

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O57 - A VISCOUS FILM SAMPLE CHAMBER FOR LASER ABLATION INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY

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Laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) is a powerful method to determine the elemental composition of solid-state samples as it combines the high sensitivity and isotope selectivity of ICP-MS detection and the simplicity of laser ablation sampling. This technique enables rapid multiple sampling of the analysed material, such as needed for mapping or in-depth profiling applications. However, the duration of these measurements is practically restricted by the time taken for the particle to be transported from the sampling point to the ICP torch. The ablation cell, i.e. the sample holder, should combine high removal rate, high efficiency (i.e. complete transport of the ablated material) and reduced memory effects. These goals may be achieved by carefully designing the geometry of the cell and its gas flow patterns. A new cell design which enables a homogeneous fast removal (around 250 ms) from a cylindrical chamber with 70 mm diameter is introduced in this paper. This result is achieved by combining a diffused, cylindrical flow pattern with an extraction tube coaxial with the laser beam and fixed to the laser assembly which enables the sampling point to be constantly positioned on the ablation spot. The lower part of the cell is mounted on the x,y stage for sample movement: the cell sealing is warranted by a viscous film junction between the lower and upper cell parts. Optimisation and performances of the apparatus are discussed in detail: performances are compared to existing designs. MIUR is gratefully acknowledged for financial contribution (PRIN project 2010AXENJ8).

O58 - NON-TARGET UHPLC-HIGH RESOLUTION TANDEM MASS SPECTROMETRY ANALYSIS OF PHOTOIRRADIATED RED BEVERAGES

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The potential impact on human health of food dyes is receiving an increasing attention of public opinion, scientists and legislators. In particular, the Regulation EC No. 1333/2008 requires that the labelling of food commercial products containing some azo dyes (among which three largely used red colorants) also includes their potential adverse effect on activity and attention in children [1]. To overcome risk to health, when possible, in food and beverages the azo dyes are being substituted by dyes of natural origin. In particular red azo dyes are being replaced by the natural Red Cochineal (Carminic acid, E120).
But the use of natural dyes does not assure food safety.
Since red azo dyes were shown to undergo photodegradation when the beverages containing the dyes were exposed to sun light irradiation [1-2], aim of this study is to evaluate if also the natural E120 shows a similar behaviour. For this purpose, sixteen beverages of different composition but all containing E120 have been undergone, in their sealed bottles, to solar box irradiation in conditions simulating natural sunlight. In all the beverages a complete disappearance of the red colour was observed.
Aim of the work was to identify degradation products common to all the beverages by using a non-target approach carried out with UHPLC-QTOF MS/MS system. Since the degradation pathway was shown to depend on beverage composition [1-2], it must be taken into account the possibility that different interaction effects take place among the different ingredients and the dye degradation pathway.
To identify for all the beverages a common degradation pathway, the use of the principal component analysis has been fundamental.
Several MS experiments have been concatenated together (TOF-scan and 10 MS/MS spectra every 0.8 s) to obtain information about the high resolution MS and MS/MS spectra of the species present.

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O59 - MALDI IMAGING OF NEUROTRANSMITTER TRANSPORTER-LINKED SIGNALING NETWORKS

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Serotonin (5-hydroxytryptamine, 5-HT) is a monoamine neurotransmitter and hormone that plays key roles in the regulation of sleep, reproduction, feeding behviour, emotion and cognition and diverse physiological functions[1]. Serotonin reuptake transporter (SERT) is a key regulator of serotonin neurotransmission by removing serotonin (5-HT)from the extracellular fluid (ECF)[1].Alterations in 5-HT transmission have beenimplicated in numerous psychiatric disorders and SERT isthe initial target for many psychoactive drugs including antidepressants [2]. In the present work SERT knockout (SERT-KO) and wild-type (WT) mice were studied in order to the identify protein changes that occur in the KO mouse when compared with WT in an area of the brain richin SERT expression, i.e. striatum. Serial coronal sections of mouse brain were investigated by MALDI mass spectrometry and Imaging Mass Spectrometry (IMS) was used to map the distribution of targeted compounds on tissue, to localize molecules and their regionalized distribution in this specific area of interest. The IMS is a technology that makes resiospecific molecular measurements directly from biological specimens[3]. Protein profiles across the coronal striatal sections wereacquired in a mass range from 2700 to 27,500 Da and the acquired spectra showed changes consistent between the animal models WT and SERT KO. The intresting result is that some ions appear to be exclusive to that striatal region. Such information has future potential as the identification proteins where expression in postsynaptic cells is contingent upon the presynaptic expression and function of these transporters.

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O60 - GREEN PHOTOCATALYTIC HYDROGEN PRODUCTION FROM OLIVE MILL WASTEWATER

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An alternative and sustainable way to produce hydrogen (H_2) by photocatalytic sacrificial water splitting on a low-cost biomass was explored. Platinized titanium dioxide was used as the photocatalyst in presence of olive mill wastewater (OMW) as the electron-donor. Preliminary experiments, aimed at investigating the influence of reaction conditions on H_2 production, showed that OMW dilution, pH, irradiation time and catalyst amount play a key role in the photocatalytic process. The method has been optimized taking care of a chemometric design, and the highest H_2 yields were achieved by using 2.0 g L^{-1} catalyst, under 4 h UV-A irradiation, at pH 2.5. The optimal dilution factor of the biomass was found to be 1:30, either with distilled or tap water. Under these conditions up to 40-45 μmoles H_2 were produced, with good inter-day precision (RSD <2%, *n*=3). The contribute by direct water splitting (omitting the biomass) resulted in low yields (<5 μmoles) and no H_2 was evolved in bare titania suspension. After irradiation, the same sample submitted to further treatments in presence of fresh catalyst proved to be able to still generate H_2 in significant amounts, this supporting OMW as an efficient sacrificial agent. The catalyst proved to preserve a large part of its activity after use, therefore it can be recycled for a further run. Experiments under simulated sunlight with dyes-sensitized platinized titanium dioxide are in progress, and from the first findings, concrete seems the feasibility of solar H_2 production.
The performance of OMW as sacrificial agent for the photocatalytic water splitting H_2 production is compared to that of model molecules such as glucose and glycerol, recognized to yield appreciable H_2 evolution [1].

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O61 - LABORATORY SIMULATION OF A GLUCOSE-INDUCED REDOX TREATMENT FOR IN-SITU REMEDIATION OF GROUNDWATER POLLUTED BY HEXAVALENT CHROMIUM

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The problem of water resources pollution by Cr(VI) has recently become increasingly important due to the toxicity and carcinogenicity of this element. The Cr(VI) released in the soil can be naturally reduced to Cr(III), however, if the reducing ability of the soil is not sufficient to transform all the Cr(VI) introduced, it may persist and be easily leached resulting in a contamination of surface and ground water. Therefore, the development of techniques for remediation is necessary, in particular for the groundwater. Nowadays the removal techniques of Cr from water can be divided in three categories: containment, ex-situ and in-situ treatments. A decontamination process should be efficient, easy and cheap.
To this end, a promising approach is the technique of bioremediation with organic nutrients, which consists in a process in-situ with the addition of sugar solution into the groundwater in order to stimulate microbial activity. In fact, in literature has reported that the reduction of Cr(VI) in the sediments occurs through complex mechanisms that primarily involves the microbial biomass.
This work aims to simulate on a laboratory scale, an in-situ glucose-mediated bioremediation treatment. A simple and inexpensive experimental configuration was used, involving a suspension of water/sediments contaminated by Cr(VI).
Dissolved oxygen, pH, and content of Cr(VI), Fe, Ni and Mn were monitored. In addition, the change of the contact time, the glucose concentration and the aerobic/anaerobic conditions was examined in order to take into account their effect on the process.
The results showed the progressive depletion of Cr(VI) when increasing the time of contact and the glucose concentration. Moreover an anoxic atmosphere was beneficial. However, after a long contact time and at high glucose concentration the release in solution of Fe, Ni and Mn was observed. Further investigation is therefore necessary to understand the complex mechanism that involves the process of reduction of Cr(VI) with to the release of other metal ions of environmental significance.

O62 - RICE HUSK AS BIOSORBENT FOR WASTEWATER REMEDIATION AND SPE PRECONCENTRATION OF FLUOROQUINOLONE ANTIBIOTICS

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Fluoroquinolones (FQs) are synthetic antibacterial agents widely employed in human and in veterinary medicine. They are considered pseudo-persistent pollutants frequently detected in natural waters at concentration levels ranging from ng L^{-1} to low μg L^{-1}, as a consequence of their extensive use coupled with their incomplete removal by wastewater treatment plants. Although the reported concentrations are well below the therapeutic level, the presence of antibiotic residues in the environment may result in the development of bacterial resistance phenomena [1].
Rice husk is an agricultural waste from rice milling industry, largely available in the south Lombardy plain and usually burnt or used as low value product. In the present study rice husk has been investigated for the removal from natural waters of Marbofloxacin (MAR) and Enrofloxacin (ENR), two FQs widely employed in cattle and swine farms near Pavia. The operating parameters affecting the sorption process (sorbent dose, agitation time, pH and organic matter) were optimized and batch adsorption experiments provided maximum adsorption capacities for MAR and ENR of 25 mg g^{-1} and 35 mg g^{-1}, respectively.
Due to their low concentrations in the environment, sample preconcentration is a basic step for FQs analytical determination [2,3]. The potential use of rice husk as solid-phase extraction (SPE) adsorbent for their quantification from environmental waters was examined as well. 500 ml of water sample was processed and the FQs quantitatively eluted with 6 mL tetrabutylammonium hydroxide 50 mM-acetonitrile (80:20) and analyzed by HPLC-FD. The efficiency of the procedure was assessed on natural waters (tap and river waters) enriched with each FQ, with recoveries from 75% to 107%.

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O63 - METAL STRATIGRAPHIES FROM ANTARCTIC MARINE SEDIMENTS: HINTS FOR PALEOCLIMATIC RECONSTRUCTIONS

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In the framework of national PNRA projects and European Projects (ESF HOLOCLIP - Holocene climate variability at high-Southern latitudes: an integrated perspective), several marine sediment cores were retrieved from the Antarctic continental margin and analyzed at the University of Florence for major and trace elements (including Rare Earth Elements - REEs) by ICP-AES technique.
Here we present the main results achieved from the chemical analysis of the cores collected in the Indian sector of the Antarctic Ocean (CB2010 A, George V Basin; WEGA 26PC12, WEGA 17PC02, WEGA 11GC03, Wilkes Basin) and in the Western Ross Sea (cJ5, Joides Basin; c20, Cape Hallett; c43, Wood Bay).
Most of the cores were analyzed for ^{210}Pb activities at the EPOC (Université Bordeaux I) and ^{14}C dating was performed by the University of Trieste, providing independent chronologies and showing that the cores cover from the last centuries (CB2010 A) to the whole Holocene (cJ5).
At the Chemistry Dept. in Florence, several elements were measured (Al, Ba, Be, Ca, Co, Cu, Dy, Eu, Fe, K, La, Mg, Mn, Mo, Na, Ni, Sc, Sr, Ti, V, Y, Yb, Zn), including some REEs and some relevant chemical paleomarkers such as Ba, Mo and Mn. At this purpose, a specific method for sample mineralization was set up, consisting of an acidic ($HF+HNO_3+HCl$) digestion in microwave oven, followed by a treatment with H_3BO_3. The method performances were tested on certified marine sediment materials (f.i. MESS-3) and recoveries were found to be always within the certified uncertainty.
The concentration vs. depth/age record of the measured elements has enlightened some relevant environmental features. As an example, the trend of the Ba/Al ratio and Ba_{excess} finely matches the one of *Fragilariopsis curta* (sea ice diatom species) relative abundance along the Holocene, suggesting that, once corrected for the crustal contribution, Ba can be used as a specific marker of bioproductivity.
This result looks particularly promising in view of an integration of climatic and environmental records coming from the ice and marine realms.

O64 - DETERMINATION OF POPs FROM COMBUSTION OF VINEYARD PRUNING RESIDUES IN CONTROLLED SYSTEM

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The development of an analytical method for the determination of three classes of persistent organic pollutants (POPs) from combustion of vine pruning residues is presented. The Italian law (D.Lgs. 205/2010) prohibits the disposal of vine pruning residues by open fire. This can turn into an opportunity to exploit this waste as an energy source. The proposed method aims at evaluating the impact in the atmosphere resulting from the combustion of the vines shoots, in order to determine if they are suitable for being used (and in which conditions) as biofuel. This work is part of a larger project: PRO.S.E.C.CO (Sustainable PROduction of Energy by Combustion and COmpost) is a research project supported by Veneto Region (measure 124 of the Rural Development Plan), coordinated by the University of Padova in collaboration with winery farms and Agencies of Conegliano-Valdobbiadene DOCG wine production area.
Chemical analyses of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzo-furans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs) were carried out. Great effort was put into creating a simple and effective method without pre-separation of these classes of analytes prior to GC analysis, in order to save time and materials. The state of the art of determination of PCDD/Fs in fly ash from waste incinerators or metallurgical plants is well described by many authors. However, very few papers deal with POPs production from agricultural residues combustion. Samples were collected, after combustion in controlled atmosphere in a medium-size wood boiler, by an isokinetic sampling line. Three matrices were collected: fly ash, condensed and gas. The fly ash samples, collected on quartz fiber filters, and the flue gas samples, adsorbed on a XAD resin, were extracted via Pressurized Liquid Extraction (PLE). The condensate samples were extracted via liquid-liquid extraction. All the three samples were purified by preparative liquid chromatography by using an automated system (Power Prep), and finally analyzed by chromatographic techniques such as HRGC-LRMS and HRGC-HRMS. First results show a significant different distribution pattern of congeners of the analytes in the three matrices in analysis.

O65 - ANALYSIS OF ORGANIC SPECIES IN AIRBORNE PARTICULATE MATTERT

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The impact of airborne particulate matter (PM) on health represents a serious scientific and policy issue [1]. Organic components contained in the organic carbon (OC) fraction account for a large share of the total PM mass. Some of them play an important role in PM health effects due to their toxicological potential impacts (e.g. PAH). In addition, certain organic compounds (organic markers) can be used for the identification of PM sources. In this study, a comprehensive assessment of PM composition has been carried out including numerous organic substances such as levoglucosa (marker of wood burning), water soluble organic carbon (WSOC), short chain organic acids, PAHs (identified as carcinogenic by IARC), fatty acids (to estimate the contribution of cooking), hopanes (related to traffic exhaust) and some SOA (secondary organic aerosol) markers. In particular, a new more rapid methodology has been set up for the quantification by GC-MS of hopanes and fatty acids. Punches taken from high volume filters were transferred in 2 mL vials and extracted three times by sonication (20 min) with 2 mL of a 1:1:1 vol/vol mixture of dichloromethane/n-hexane/methanol. The organic fractions were collected and taken to dryness *in vacuo*. Each sample was derivatized with 400 μL of MeOH saturated with HCl_g (T= 42 °C, 40 min) and the analytes extracted 3 times with 600 μL of n-hexane. The organic phases were collected and reduced to 600 μL; 1μL analyzed by GC-MS (Bruker SCION SQ). The recovery (97.21 ± 2.45%) was evaluated by internal standard addition. Different classes of contaminants, such as hopanes (on average 1.09 ± 0.02 ng/m^3), phthalates (on average 6.31 ± 0.29 ng/m^3), and PAH (on average 7.90 ± 0.43 pg/m^3) have been quantified. Paraffins, fatty acids and triglycerides were also identified. This analytical approach proposed was applied to the analysis of PM10 samples collected from June 2011 to December 2012 at the JRC ABC-IS site (http:abc-is.jrc.ec.europa.eu) in Ispra (Italy) with the double aim of carrying out a source apportionment study applying the European protocols and to deepen the knowledge on SOA formation.

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O66 - FEASIBILITY OF DIRECT-EI LC-MS AS A TOOL FOR FOOD SAFETY APPLICATIONS: IDENTIFICATION AND QUANTITATION OF ENVIRONMENTAL CONTAMINANTS IN MILK POWDER.

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Raw materials coming from developing countries are increasingly used in food industries due to their low cost. Sometimes, these ingredients are not subjected to severe safety controls in the countries of origin. This represents a great concern when food preparation is involved. It is mandatory to have efficient and sensitive analytical methods to detect food contamination. We present the feasibility of Direct-EI/LC-MS instrumentation to determine some environmental contaminant residues in milk powder. This technique is matrix effect free and gives full EI mass spectra of the analytes for unparallel identification. To demonstrate the feasibility, reconstituted milk powders were spiked with an environmental contaminant standard mixture. The samples were extracted via QuEChERS methodology and SPE for comparative purposes. Spiked and blank sample extracts were separated on a nanoAcquity UPLC column, 1.8µm, (0.075 mm x 150 mm) with a flow rate of 300 nL/min. The column was coupled via Direct-EI to the ion source of an Agilent 5975C MSD. Signal was collected in full scan- and SIM-modes for qualitative and quantitative analyses. Linearity, limit of detection, precision, and accuracy were determined for method validation. Twelve compounds belonging to the classes of phenols, estrogens, carbamoyloxime, triazine, methylcarbamate and phenoxy acids have been considered. They are all involved in food contamination and present difficulties in high resolution, accurate mass ESI-LC/MS identification due to the number of isobaric compounds in a ChemSpider search, for example: diethylstilbestrol returns over 900 entries with its exact mass. The mass spectrometer was operated in SIM-mode for specificity and to maximize signal response. Instrumental limits of detection are in the range of 0.35-5 ng that correspond to method limits of detection ranging from 7 to 100 ppb due to a pre-concentration step during the QuEChERS extraction and from 0.07 to 1.0 ppb due to a pre-concentration step during the SPE method. Recoveries and matrix effects evaluation will complete the method validation. Real samples will be analyzed to confirm the usefulness of the method.

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O67 - COMPREHENSIVE STUDY OF PCBs BEHAVIOUR IN A ION TRAP MASS SPECTROMETER AND OPTIMIZATION OF INSTRUMENTAL PARAMETERS FOR TANDEM MASS ANALYSIS

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This work presents a comprehensive study on polychlorobiphenyls behaviour in fragmentation processes into an ion trap mass spectrometer and provides the basis for the development of reliable and cost-effective methods to be routinely applied to the determination of ultra-low level of PCB congeners in different sample matrices. PCBs selected for this study are of major relevance in environmental and toxicological fields [1] and cover the full range of structural characteristics of this class of compounds. A clear relationship between structure and behaviour of PCBs in MS/MS experiments has been observed; in particular congeners show different stability and follow different fragmentation mechanisms according to the number of chlorine atoms in ortho position of biphenyl system. The different behaviours of mono-*ortho*-, non-*ortho*- and di-*ortho*- PCB congeners as function of collision induced dissociation parameters has been highlighted. Overall data demonstrate that di-*ortho* congeners show lower thermodynamic stability and higher fragmentation rate than non/mono-*ortho*. Experimental kinetic curves of mono/non-*ortho* and di-*ortho* congeners follow classical first order kinetics curves; in particular di-*ortho* congeners follow a first order consecutive reaction while mono/non-*ortho* follow a first order parallel reaction. For each congener the kinetic constant of fragmentation of the molecular ion has been determined. Data obtained give a new contribution to the understanding of PCBs transformation paths in environmental and biochemical fields [2, 3]. Results comply with data reported in literature [4, 5] about environmental persistence and bioaccumulation in living systems providing a key to their interpretation. The general picture of PCBs behaviour inside an ion trap mass spectrometer, obtained by the systematic trends observed in fragmentation processes according to chlorine position in the biphenyl system, allows to establish a basis for the development of high performance analytical methods for the determination of any PCB. Results have been applied to the optimization of instrumental parameters in order to build an analytical methods in GC/MS for PCBs in seawater at ultra-trace concentration levels. Full method validation is reported. Particular attention has been paid to limit of detection determination.

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O68 - THERMAL DEGRADATION STUDIES OF ULTRA-THIN POLYMER FILMS BY ONLINE TGA-GC-MS ANALYSIS.

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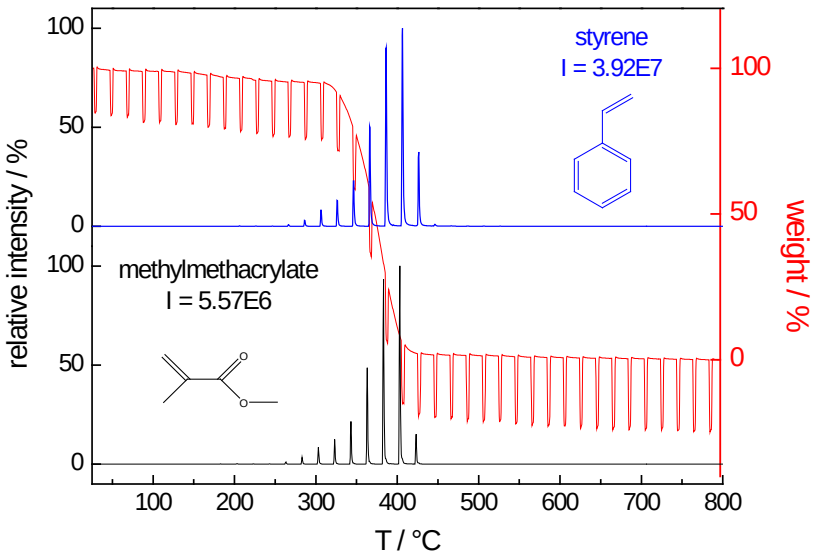
This study addresses the thermal stability and degradation path of symmetric and asymmetric PS-*b*-PMMA block copolymers, widely employed to generate templates for nanopatterned materials, and of the associated PS-*r*-PMMA random copolymers, through a combination of TGA and TGA-GC-MS techniques under isothermal and dynamic conditions. The thermal stability was studied by the analyses of the evolved gas from TGA that was transferred to a GC-MS using an automatic interface consisting of three components: a heated transfer-line (HTL1) from TGA to an automatic gas sampling system (autoinjector), an autoinjector (AI) equipped by a switch valve and a prefixed volume loop and a second heated transfer line (HTL2) from the AI to the GC-MS injector port. The automatic AI controls the repetitive pulsed transfer of known amounts of the evolved gas, with the desired frequency, in the injector of the GC-MS system. The above reported technique proves to be adequate to characterize the thermal behavior of macro system as the bulk materials, micro system as thick films (few μm of thickness) and nano system as ultra-thin film (few nm of thickness).



TGA GC-MS scan in bulk for a PS-*r*-PMMA copolymer

O69 - AMPEROMETRIC MINIPLATFORM FOR ISOPROPYL-9H-THIOXANTHONE DETECTION BASED ON MOLECULARLY IMPRINTED POLYMER

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Isopropyl-9H-thioxanthone (ITX) is a mixture of 2 or 4 isomers, widely used in inks and varnishes for food packaging as a radicalic UV initiator in dark pigmented inks [1]. Due to migration from the packaging, and despite of its low solubility in water, it can contaminate liquids containing solid particles or micelles, as for example milk and fruit juice. A constant control of the ITX content particularly in baby food is required. In the present study, the possibility of determining ITX by a specific sensor based on electrochemical transduction is investigated, even if ITX is not electroactive.

The proposed sensor is based on a Molecularly Imprinted Polymer (MIP) in direct contact with a carbon surface (glassy carbon, graphite, graphite ink), which acts as a selective receptor for ITX. Even in very diluted aqueous solutions a small electrical current flows, due to the ions present in the polymer [2]. In the case here considered, they are negatively charged carboxylic groups permanently linked to the polymer, and positively charged mobile counter ions. The flowing current is modulated by the combination of the analyte with the receptor sites present in the MIP phase, which in turn depends on the ITX concentration in the sample solution. The specific rebinding of the template to MIP assures the selectivity.

In the case of the MIPs here considered, the current measured at -0.850 V (vs Ag/AgCl) and 0.5 s is inversely proportional to the ITX concentration from 0 to 1 ppm (the solubility of ITX), with well reproducible ordinate at the origin and slope. The detection limit was around 50 ug/l, at the limit required by the presently recommended values [1]. The selectivity for ITX with respect to similar substances as thioxanthone and 1-chloro-4-propoxy-9H-tioxanthen-4-one (CPTX) is very good.

Similar results were obtained using a screen printed three electrodes platform, which was considered for the sake of miniaturization.

This work shows the possibility of realizing a marker-free electrochemical sensor for a not electroactive substance, with an acceptably low detection limit.

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O70 - ALLOSTERICALLY-TUNABLE, DNA-BASED SWITCHES TRIGGERED BY HEAVY METAL

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DNA has become the material of choice for the construction of complex nanometer-scale molecular structures. Recently, the possibility of transforming these elegant nanostructures into active "addressable" "nanomachines" that respond to specific molecular inputs (analytes or even "fuels") has been also demonstrated, opening up applications ranging from drug-release vehicles to autonomous molecular robots.
In order to couple input recognition to structural motion, which in turn can be coupled to a range of outputs (e.g. fluorescence, electrochemistry, drug release, catalysis), DNA switches are designed to flip from a *non-binding* conformation to a second, *binding-competent* conformation upon binding to a specific molecular input [1]. An advantage of DNA-based switches is the wide range of effectors that can be used to trigger such switching, including complementary nucleic acid strands as well as small molecule or protein targets through the use of, for example, aptamer sequences [2]. A second advantage is the ease with which secondary effectors (ligands that bind distal sites on the switch) can be used to regulate their activity via an effect called "allostery". This potentially valuable effect, however, has seen relatively less attention in the DNA-design literature [3]. In response, we report here the rational design of allosterically tunable, conformation-linked DNA switches triggered by specific heavy metal ions.

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O71 - AGENT ORANGE HERBICIDES, ORGANOPHOSPHATE AND TRIAZINIC PESTICIDES ANALYSIS USING NEW ORGANIC PHASE IMMUNOSENSORS

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The determination of traces of pesticides in edible oils is an important problem. In fact several kind of pesticides are scarcely soluble in aqueous solutions, in addition also the oily matrix is practically insoluble in aqueous solvent, therefore the quantitative determination of these species in oily matrices has always posed a serious problem only partially solved by such techniques as gas chromatography, which are more suitable when employed in a laboratory than in situ. A substantial contribution to solving this problem was the development of Organic Phase Enzyme Electrodes (OPEEs), i.e. enzymatic electrodes capable of operating in organic solvents [1] and that can also act in situ. One classical example is that of inhibition OPEEs [2] to analyse different types of pesticides that are relatively insoluble in aqueous solution, in the development of which also our team was recently involved [3]. The drawback consists in the fact that it is often complained that inhibition biosensors are relatively unselective also versus pesticides belonging to different phytopharmaceutical classes. Immunosensors, on the contrary, are the most selective biosensors. However, in the last year we developed a new organic phase Immuno Electrode (OPIE) [4]. Using this new device, applications were developed first of all to detect triazinic pesticides in extra virgin olive oil, obtaining good results [4]. Therefore new applications were recently developed using the novel OPIEs to detect other herbicides and pesticides such as 2,4-D and 2,4,5-T (i.e. agent orange herbicides), atrazine and simazine (triazinic pesticides) and parathion (organophosphate pesticide) both in olive and in sunflower oil. The working conditions were studied and optimized for new OPIE in the first previous research on the triazinic analysis containing in extra virgin olive oil [4]. For the analysis of the same pesticides in sunflowers oil, the only condition changed was the use of 75% V/V n-hexane/chloroform mixture, which replaced the 50% V/V mixture of the same solvents used in the previous research [4] and employed in the competition step of the immunological method. This was because of the better solubility of sunflower oil in the first mixture than in the latter. For all the pesticides studied also the values of the affinity constant were estimated on the basis of the value of the concentration at which half of the maximum response was obtained. k_{aff} were found to be of the order of 10^6 M^{-1} in all cases.

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O72 - PYROLIZED PHOTORESIST CARBON ELECTRODES: APPLICATION TO HEAVY METAL ANALYSIS

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The preparation of a novel kind of carbon electrodes obtained by photolithographic microfabrication and pyrolysis of an epoxy-based photoresist named SU-8 [1-2] is studied and optimized. SU8 derived carbon tends to be glassy in nature however, based on the fabrication and pyrolysis strategies one can obtain a range of electrical, electrochemical and thermal properties related to the tuning of the graphitic content of the thus obtained carbon. To this aim, the electrochemical behavior of pyrolized photoresist carbon electrodes (PPCEs) is examined as a function of the pyrolysis time and SU8 film thickness. The results of the electrical, spectroscopic and difrattometric characterization of the PPCEs are reported and discussed with reference to the observed voltammetric performances.

Finally, the PCCEs are applied to the determination of heavy metal ions. To this aim, Bi-modified PPCE are used to analyze trace concentration of Cd(II) and Pb(II) via anodic stripping voltammetry (ASV) and Ni(II) by adosorptive cathodic strpping voltammetry. PPCE modified with gold nanoparticles are developed for performing the ASV of trace As(III). For all the analytes detection limits as low as 1 μgL^{-1} are obtained, using a preconcentration time of only few minutes, so opening new prospects for the development of deployable electroanalytical chips.

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O73 - PROTECTIVE COATINGS INFLUENCE ON OXYGEN OPTICAL SENSORS SIGNAL

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Determining oxygen both in gaseous and aqueous media is a claimed main feature of oxygen optical sensors based on luminescence quenching of a suitable luminophore, but environment may alter the sensor signal due to reflection and refraction variation on the interface, so that sensors become unreliable if water condense (in gas phase) or gas bubbles (in aqueous medium) are present. A suitable optical insulation is sometimes employed even in commercial sensors in order to overcome those problems, but up to our knowledge there are no studies about it in literature yet.
The light intensity detection-based sensors, recently been proved as robust as the more expensive, lifetime detection-based, ones [1], are based on a membrane prepared embedding 5,10,15,20-Tetrakis(pentafluorophenyl)-21H,23H-porphine Platinum(II) (PtTFPP) in either polysulfone or polystyrene supporting matrixes. White diffusive coatings were employed to increase light intensity read by the detector. Various paints were sprayed and spin coated on the sensing membranes, achieving up to a very large seven-fold increase of the signal to noise ratio. Black silicone paints superimposed to the white one avoided environment light interferences. Coatings allowed the sensor to be used indifferently for dissolved and gas phase oxygen determination.

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O74 - ELECTROANALYTICAL APPLICATIONS OF A CARBON-Au NANOPARTICLES COMPOSITE INCLUDED IN A SOLGEL MATRIX

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The use of Au nanoparticles (AuNPs) in electroanalysis has attracted the interest of scientific community due to properties such as activation of electrocatalytic processes and antifouling. Despite the large number of strategies proposed for stable deposition of AuNPs onto electrode systems, the main common drawback of electrode coatings lies in the necessity of a periodic film regeneration. As a matter of fact, this process is time consuming and often limits the reproducibility of the electrode responses obtained with different coatings. In this respect, bulk sol-gel electrodes are specifically developed to overcome this limit: the rigid inorganic matrix can stably incorporate different components active with respect to the charge transfer and their surface can be very simply and rapidly renewed by means of mechanical cleaning procedures. Graphite grains are generally also included in the sol-gel material to induce the conductivity degree necessary for their use in amperometric analysis.
We could verify here that the impregnation of graphite grains with pre-synthesised AuNPs constitutes a valid approach to stably fix a high amount of AuNPs in a stable inorganic matrix, even characterised by a rapid surface renewal. As verified by TEM images, AuNPs fixed on carbon grains surface maintain their individual nature, constituting the basic feature for exerting their electrocatalytic and antifouling properties at best.
The electrodes realised have been characterised through morphological and electrochemical investigations, demonstrating the uniform distribution of AuNPs on the surface and at different depth inside the bulk. Finally, electrochemical tests carried out on the cathodic reduction of H_2O_2 and the anodic oxidation of glucose demonstrate the electrocatalytic activity of the AuNPs, the high repeatability of the responses obtained and the reproducibility of the electrode systems, simply restored by routine mechanical cleaning procedures. Quite interestingly, at variance with many non-enzymatic electrode systems developed for glucose determination, the sensor proposed is suitable to be used even at the physiologic neutral pH. Finally, preliminary tests carried out either in glucose or in fructose solutions demonstrate that the two analytes can be separately quantified from a mixture of them.

O75 - GOLD NANO-PARTICLES-PEPTIDE BASED GAS SENSORS ARRAY: COMPUTATIONAL STUDY AND PRACTICAL APPLICATIONS

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In recent years, peptide have demonstrated to be a very useful tool for sensors surface modification. Different approaches were proposed working both in liquid and gas phase [1].
One of the most interesting features of peptides as sensing molecules is due to the large number of possible structure combination that can be obtained.
In this work a practical application of a peptide-based electronic nose to chocolate is proposed in order to discriminate off-flavoured samples from regular ones. In this application seven different peptides, with different length and amino-acid sequence, were used as modifying moieties. They were not designed on a specific purpose. To evaluate the possibility of doing this, a computational study was carried out on five of the seven peptides used for real samples, and virtual data were compared to experimental ones.
For real samples measurement, peptides were covalently bonded to Gold Nano-particles (GNPs) and then deposited on 20 MHz quartz crystal microbalances. Samples were placed into glass vessels and incubated at controlled temperature; head-space was then carried to the measurement chamber (containing the GNP-peptide based gas sensors array) through a Nitrogen flow. A tubing system with three-way stop-cocks allowed to divert the flow through the sample head-space or directly to the measurement chamber for baseline evaluation.
In the computational study, simulated affinity binding properties of the 5 studied peptides versus 14 volatile compounds belonging to relevant chemical classes were evaluated. The same 14 volatile compounds were then analyzed with the gas sensors array containing the same five peptides. Data were compared on the basis of a two-tailed T-test analysis. Considering the entire dataset, virtual and experimental results matched in 70% of cases. Best results (up to 93%) were obtained with longest peptides. Molecular modeling approach was proved to be a convenient tool in predicting the behavior of sensors array for gas detection.

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O76 - SCREEN-PRINTED ELECTRODES MODIFIED WITH NANOSTRUCTURED CARBON BLACK AS PLATFORM TO DEVELOP SENSORS AND BIOSENSORS

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Carbon black is widely used as carbon material to construct sensors for the detection of analytes in gaseous phase and for the development of fuel cells and sodium-ion batteries. However, until 2012, few applications have been reported using carbon black as electrode material for analyte detection in solution [1-3]. In this work we demonstrated the possibility to use screen-printed electrodes (SPEs) modified *via* "film" deposition with a stable dispersion of nanostructured CB as platform to develop biosensors and also to produce sensors modified with electrochemical mediators. In the first case the good sensitivity towards thiocholine was used to develop a cholinesterase biosensor for organophosphorus pesticides immobilizing the butyrylcholinesterase via cross-linking. The biosensor produced was characterised by Electrochemical Impedance Spectroscopy and Scanning Electron Microscopy. The biosensor was challenged in standard solutions of paraoxon-ethyl obtaining a linear range up to 30 ppb with a detection limit of 5 ppb. The biosensor was also challenged in waste water samples obtaining satisfactory recovery values. In the second case, a nanocomposite with CB and electrochemical mediator Prussian Blue (PB) was also developed using a "bilayer approach" on the surface of the working electrode, or using a dispersion of CB previously modified with PB (CB/PB). This sensor modified with the dispersion of CB/PB was applied for H_2O_2 detection showing LOD (0.3 μM) lower than the one (1 μM) obtained with SPE modified with only PB. The novel sensor was applied for H_2O_2 detection in the spiked swimming pool water samples with satisfactory accuracy. This work confirms the potentiality of CB in electrochemical sensor field demonstrating that can be an alternative to common carbon nanomaterials used such as carbon nanotubes with the advantage to be cost-effective (around 1 euro for 1 kg).

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O77 - COMPOSITE ELECTRODES BASED ON NANOTUBES/ POLYDISPERSED METAL PARTICLES. A VOLTAMMETRIC AND MORPHOLOGICAL STUDY.

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The electroanalytical performance of the amperometric sensors expressed in terms of current density, low values of applied potentials, temporal reproducibility, sensitività and selectivity, are related at the particular electrode design, surface morphology and redox mediator used. As consequence, many studies were proposed regarding the characterization of chemically modified electrodes (CMEs) with particolar redox mediators nanostructured on the electrode surface and dispersed in conducting perm-selective polymers, alloys of transitinon metals or their mixing oxides, etc. [1]. Carbon nanotubes (CNTs), are supposed to be a key component of many technologies because of their outstanding structural, mechanical and electronic properties. They are microscale length graphene tubes with end "caps" consisted either of one graphitic layer and 1-2 nm in diameter (SWCNT), or of two or more graphitic layers with interlayers spacing of 3-4 nm and diameters of 2-20 nm (MWCNT). These materials are recently studied and proposed for the preparation of chemically modified electrodes in various electrochemical contexts [2-5]. In fact, these materials can be employed for a wide range of applications [6] such as: optical and electronic devices, electrochemical energy conversion and storage, etc.
The present communication regards an electrochemical and morphological study of CMEs based on MWCNT/Au e MWCNT/Rh obtained by a direct casting process of Au particles or by electrodeposition of rhodium species on the CNTs structure. The resulting CMEs were characterized towards the electrooxidation of some carbohydrates in alkaline medium or by electroreduction of nitrate species in acid solutions. The morphological investigation by AFM technique (atomic force microscopy), supports the investigation in order to characterize the CMEs as potential sensing probes in electroanalytical contexts.

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O78 - CAVITAND-BASED MATERIALS FOR THE DETERMINATION OF NITROAROMATIC EXPLOSIVES AND EXPLOSIVE TAGGANTS

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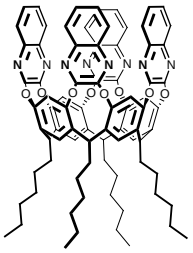
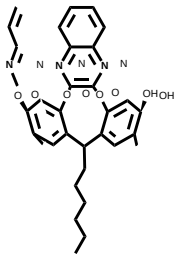
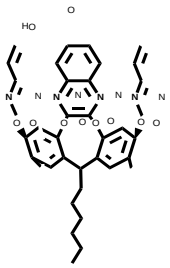
Recently, homeland security has emerged as priority area of action, thus requiring the development of reliable, selective and rapid analytical tools to be applied for in-situ monitoring[1]. Cavitands, synthetic organic compounds having enforced cavities of molecular dimensions, are the ideal candidates for the functionalization of appropriate materials to be used as devices in the sensing of specific classes of analytes[2]. In the present work three different quinoxaline bridged cavitands, namely 4 Qx-Cav, 3Qx-Cav and 4QxCOOH-Cav were synthesized and used as solid-phase microextraction coatings for the determination of nitroaromatic explosives and explosive taggants.



4Qx-Cav



3Qx-Cav



4QxCOOH-Cav

4QxCOOH-Cav proved to be the cavitand of choice for the detection of nitroaromatic explosives obtaining GC responses 2-20 times higher than those achieved using 4Qx-Cav, 3Qx-Cav and commercially available devices. A thermal stability until 450°C, a coating thickness of 50±4 μm (n=3) and a very good intra- and inter-batch repeatability with RSD lower than 5% were additional features of the developed coating. Finally, detection limits values in the low ng/l range allowed the determination of nitroaromatic explosives and explosive taggants at trace levels in samples of forensic concern.

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O79 - EXTRACTION STRATEGIES FOR THE DETERMINATION OF DRUGS OF ABUSE IN BIOLOGICAL MATRICES

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In biological analysis, sample preparation is the most important issue: it is still a critical and time-consuming step that typically takes 80% of the total analysis time. For the determination of drugs of abuse in biological matrix, each one (blood, urine, oral fluid, hair) presents different challenges and requires specific clean-up procedures also taking in account the selected detection technique. LC-MS(/MS) is considered to be the benchmark for quantitative/qualitative bioanalysis, providing suitable specificity, sensitivity to the method, but matrix effect could affect the analysis.
Different techniques have been developed for the clean-up of biological samples, which offer considerable advantages compared to conventional ones, considering the matrix to analyze, the complexity and the concentration of target analytes (parent drug or metabolites), which may be quite different.
One important issue has been the miniaturization of SPE (µ-SPE) by means of micro-tips for the determination of illicit drugs belonging to different chemical classes in saliva, plasma and urine [1,2]. Another strategy for reducing sample volume has been the development of MEPS extraction for the determination of cannabinoids in oral fluids at very low concentration levels [3]. Pressurized liquid extraction (PLE) has been chosen for the extraction of analytes from hair: drugs of abuse belonging to different classes have been successfully extracted and the whole procedure had been fully validated [4]. Another strategy has involved computational design of peptide ligands as SPE sorbents for the determination of cocaine and metabolites in plasma and urine [5].

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O80 - CHEMOMETRIC APPROACH TO OPEN VALIDATION PROTOCOLS. PREDICTION OF VALIDATION PARAMETERS IN UHPLC-MS/MS METHODS FOR LARGE SETS OF ANALYTES

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Analytical methods based on ultrahigh-performance liquid chromatography – tandem mass spectrometry (UHPLC – MS/MS) nowadays allow the simultaneous determination of hundreds of target analytes. The traditional approach to quantitative method validation has three major drawbacks, namely (i) it is extremely laborious, repetitive and rigid; (ii) it does not allow the introduction of new analytes without starting the validation from the very beginning and (iii) it is performed on spiked blank matrices, whose very nature is considerably modified by the addition of a large number of candidate analytes standard solutions.
Predictive chemometric models were developed from closed sets of analytes for the estimation of validation parameters on molecules of the same class, but not included in the training set. Retention time, matrix effect, recovery effect, identification (LOD) and quantification (LOQ) limits were predicted with Principal Components Analysis (PCA) and Partial Least Squares (PLS) methods. These procedures were initially applied to data previously reported in validated UHPLC-MS/MS multi-residue methods for human whole blood [1], oral fluid [2] and urine [3] samples, proving effective and in accordance with the recommendations of SOFT/AAFS guidelines. Secondly, a new validation procedure was developed for UHPLC-MS/MS multi-residue methods based on the concept of robustness, allowing a rapid and complete evaluation of the validation parameters required by international guidelines. Our protocol suggests to examine samples prepared with coeluting and non-coeluting analytes, in order to verify electrospray (ESI) signal suppressions phenomena and interferences in realistic situations, in opposition to fully spiked blank samples at concentrations comprised by standard validation practices. Lastly, chemometrically-driven validation processes are proposed for new analytes to be included into existing validated methods, together during typical validation practices.

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O81 - PLASTIBODIES INSTEAD OF ANTIBODIES? TOWARDS WORKING ENZYME-BASED MOLECULARLY IMPRINTED SORBENT ASSAYS (E-MISAS)

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Molecularly imprinted polymers (MIPs) are smart polymeric receptors able to mimic the specific molecular recognition phenomena present in living systems. They have attracted much interest and have found applicability in a number of research areas, such as stationary phase for chromatographic separations and affinity solid-phase extraction, catalysis, controlled drug release and sensor technology.
People who working the field of molecular imprinting often describe these materials as “plastibodies”, a sort of artificial antibodies which share with natural antibodies the same binding behaviour. In fact, MIPs show a set of properties apparently very similar to those of natural antibodies (immunoglobulins): a marked binding selectivity towards the related ligands and binding properties raising form multiple reversible non-covalent interactions, characterized by well-defined binding thermodynamics and kinetics. It is therefore not surprising that MIPs can be potentially used as artificial replacement of antibodies in diagnostic assays in the so-called “molecularly imprinted sorbent assay”.
In this communication, we present our experimental approaches to developed new (pseudo)immunoassays for peptide targets based on the use of "plastic antibodies”. Although some pseudoimmunoassays exploiting MIPs have been described, the adaptation of enzyme-linked immunoassays to MIPs has achieved only a very limited success and so far have not allowed the development of working ELISA-like methods.
With the aim of establishing an ELISA-like assay based on the use of molecular imprinted polymers, MIPs with recognition properties towards peptides were directly synthesized into polystyrene wells of microtiter plates. MIPs, covalently attached to polystyrene, played the role of immobilized antibodies. Assays with the template, labeled with peroxidase (pp-HRP)were carried out to evaluate binding properties of several “plastic antibodies”. The optimal MIP clearly demonstrated selective binding of the pp-HRP. Moreover, competitive experiments carried out in the presence of the target peptides proved that the MIPis also able to recognize these molecules. The experimental results allowed us to conceive the development of an effective enzyme-based moleculalry imprinted sorbent assay (E-MISA) to effectively quantify peptides at levels of clinical relevance.

O82 - BIOLUMINESCENCE HELPS MALARIA RESEARCH: EXPLOITING NEW LUCIFERASES TO IMPROVE ANALYTICAL PERFORMANCE OF ANTIMALARIAL SCREENING ASSAYS.

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In the renewed efforts to combat malaria, substantial improvement of bioanalytical tools are needed to tackle the key step of parasite transmission at different stages. Success of the most effective antimalarial drug artemisinin relies on the unique ability to kill early asexual parasites, but reports of *P. falciparum* reduced susceptibility to this drug urgently calls for drug screening assays to identify novel effective antimalarials.
P. falciparum gametocytes represent the sexual forms of the parasites that develop within the host erythrocytes. The lack of reliable assays to screen compound libraries for gametocytocidal activity prompted us to develop novel reporter cell-based assays exploiting the multiplexing and imaging potential of luciferases. First, novel red and green-emitting luciferases expressed for the first time in malaria parasite have been cloned under the control of gametocyte specific promoters and successfully integrated in the parasite genome. Four luciferases were selected thanks to their high signal to background ratios (two orders of magnitude compared to conventional wild-type luciferase) and glow type emission kinetics.
We report for the first time a single cell bioluminescence imaging assay for transgenic gametocytes performed with an optical microscope (40X magnification) equipped with an ultrasensitive EM-CCD camera.
Then we developed a dual reporter assay (DR-GAM) designed to identify compounds blocking gametocyte development at an early or a mid-late stage of maturation, measuring activities of two luciferases emitting at different wavelengths driven by gametocyte-specific promoters. Transgenic parasites were used in validation assays using artemisinin derivatives; preliminary data suggest that the selected luciferases are likely to represent promising novel tools in malaria drug screening and discovery.
This assay will be used to screen the "malaria box" of 400 newly identified antimalarial compounds from Medicines for Malaria Venture.

O83 - SOLUTIONS FOR FORENSIC TOXICOLOGY USING LC-HRMS WITH INTUITIVE DATA PROCESSING TOOLS

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Using LC-MS for forensic toxicology has drastically increased over the last 10 years, and is now widely used for both qualitative and quantitative analysis. LC-MS allows you to analyze a wider molecular weight and polarity range of compounds with better sensitivity, reduced sample preparation, and no derivatization, in less time. Conventional multi-target forensic screening methods are based upon triple quadrupole technology. However, these methods are limited to target compounds, and do not allow a retrospective analysis of collected data.
With the recent introduction of high resolution mass analyzer you have the power of accurate mass combined with an high-speed acquisition: the results are sensitivity and high-resolution MS/MS to make high throughput accurate mass screening and quantitation available to all the forensic and toxicology laboratory.
Combining all these data acquired with a powerful software tools that, together, simplify the setup of screening applications enables even high-volume labs to perform truly comprehensive screening for large numbers of both target and non-target compounds. Using LC-HRMS technology for the screening of forensic analytes allows you to retain all spectral data, not just your original range of interest. That means you can refer back to your data anytime to investigate samples further – without reruns, which are challenging with small-volume forensic samples.

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Posters

P01 - ELECTROCHEMICAL IMMUNOSENSOR FOR HEPATITIS A DETERMINATION

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Outbreaks of water-borne (*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 enteric viruses in the irrigation and housing water. In addition, there will be no official method for the detection of these viruses. Today the purification of drinking water and adequate treatment of raw sewage are the only means for the control and prevention of diseases resulting from virological contamination of water, as that due to *Hepatitis A* (HAV). Currently, the environmental presence of this 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 antibodies.
The goal of this work is the development of a rapid and low-cost analysis detection of *Hepatitis A* (HAV) in different matrices, such as water and sewage. This study represents the starting point of the development of a disposable electrochemical immunosensor for the direct determination of viral antigens in food matrices and/or in the environment. This device can be coupled with a portable instrument to perform measurements directly in the field.
We propose an electrochemical immunosensor, based on competitive enzyme-linked immunosorbent assay (ELISA) format using screen printed electrodes. Results showed a detection limit of $1 \cdot 10^{-5}$ IU/mL with a working range between $2 \cdot 10^{-5}$ – $2 \cdot 10^{-3}$ IU/mL. The proposed system was applied to sewage, wells and drinking water. The results obtained on real samples by the proposed immunosensor were compared with those of the qRT-PCR analysis, technique routinely applied by the controllers in the evaluation of these contaminated matrices by enteric viruses.

P02 - CHROMATOGRAPHIC CHARACTERIZATION OF PROPOLIS SPECIMENS FROM CALIFORNIA AND OREGON

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Propolis is a product of the beehive that bees manufacture by mixing their own wax with resins of vegetable origin. Bees collect these resins from different species of trees or bushes depending on the flora available in their area. Propolis from different parts of the world thus display a very different chemical profile [1]. Propolis is very popular in folk medicine and is accredited of many beneficial properties [2]. Nevertheless, it may cause allergic reactions in a significant part of the population [3]. The most common allergenic compounds in propolis are some caffeates and other esters- benzyl cinnamate and benzyl salicylate [3]. In the present work, the chemical profile of some propolis specimens from locations of California and Oregon has been studied. The results have been used to assess the botanical origin and the presence of allergenic species of the specimens.
The balsamic fraction has been characterized by different chromatographic techniques –HPLC, GC/MS of TMS derivatives, GC/MS of hexanic extracts, GC/MS of headspace volatiles. The quatitative analysis of caffeic acid esters was made by HPLC, the analysis of benzyl cinnamate and benzyl salicylate by GC/MS following a literature protocol [4].
All analyzed specimens contain resins from poplars of *Tacamahaca* section, typical of the western part of North American continent [5]. Nevertheless, only two specimens are pure in this sense. In all other specimens these resins are mixed with resins from poplars of *Aigeiros* section.
These two types of propolis are different in their allergenic content. Main allergen in *Tacamahaca* poplar resins is benzyl salicylate, that is actually abundant in all specimens. But pure *Tacamahaca* specimens contain no caffeates, that on the contrary are abundant in specimens that contain *Aigeiros* poplars resins. This implies that the two types of propolis may induce different allergic reactions, both in type and in strength. Strict surveillance is thus requested on propolis products from this area.

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P03 - RAPID DETECTION OF VIABLE AND NON-VIABLE PATHOGEN BACTERIA BY A MOS-ARRAY OLFACTORY SENSOR COMBINED WITH FIELD-FLOW FRACTIONATION TECHNOLOGY

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In this work, an integrated sensing system is presented for the first time, in which a metal oxide semiconductor (MOS) sensor-based electronic olfactory system (MOS-array) is assisted by the separative technique gravitational field-flow fractionation (GrFFF) module to prepare enriched fractions of bacteria from complex matrices for their analysis [1. 2]. Herein, the GrFFF-MOS integrated system is applied to the analysis of milk samples and its ability to identify pathogen bacteria (*Escherichia coli* O157:H7 and *Yersinia enterocolitica*) is evaluated. In particular, the ability of the system to independently detect two bacterial strains simultaneously present in a milk sample, as well as its ability to distinguish between viable and non-viable cells of the same strain was demonstrated for the first time. Preliminary GrFFF fractionation of contaminated milk samples provided fractions enriched in the bacterial strain of interest, which were readily available for MOS-array analysis. The MOS-array signals were then analyzed employing a chemometric approach using principal components analysis (PCA) for a first data exploration, followed by a classification method, in which PCA scores are employed as variables to perform discriminant analysis (PCA-DA) to build a model.
When artificially contaminated milk samples were analyzed upon proper system training, a 92% ability of correct prediction was obtained for *E. coli* O157:H7 and *Y. enterocolitica* mixtures, while 100% values were obtained for discrimination of viable and non-viable bacteria of the same strain. Obtained results show that GrFFF band slicing before MOS-array analysis can significantly increase reliability and reproducibility of pathogen bacteria based on their volatile organic compounds (VOC) production, simplifying the analytical procedure and largely eliminating sample matrix effects.
The developed GrFFF-MOS integrated system can be considered a simple straightforward approach for pathogen bacteria identification directly from their food matrix.

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P04 - PEPTIDE PROFILING IN CHEESE SAMPLES BY LC-TANDEM MASS SPECTROMETRY

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Proteolysis phenomena in cheese are a complex series of events leading to modifications in texture and flavor, both directly by the formation of peptides and free amino acids associated with development of desirable or undesirable taste and aroma, and indirectly by producing substrates for secondary biochemical reactions. The rate and extent of proteolysis is determined by several enzymatic activities coming from various sources, such as endogenous milk proteases, milk clotting enzymes, starter culture, contaminating microflora, etc., as well as technological food processing. Accordingly, dairy products can contain hundreds of different peptides at different levels of concentration. During the last years, several reviews and papers have been published on the analysis of intact milk proteins or peptides released from milk proteins in a wide variety of food products by Liquid Chromatography and Mass Spectrometry [1,2].
In this work, a novel bioinformatics approach coupled with nanoLC and electrospray ionization ion trap mass spectrometry is described for the identification of the oligopeptide fractions in Fior di Latte and cream cheese samples. The proposed method is based on scoring distribution associated to the protein hits at the top of each protein view report, originating from the database search of the complete LC-MS/MS run and followed by a refined identification by focusing on selected time-segments corresponding to the most intense peaks. This strategy allows the characterization of the most relevant peptides and minimizes the risk of false-positive identifications, reducing analysis time and costs, with the advantage of obtaining a lot of important information by a single LC-MS/MS run.

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P05 - ANALYTICAL STRATEGIES FOR THE NON INVASIVE ANALYSIS OF LACTATE IN SPORT AND CLINICS.

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The measurement of lactate in biological fluids is an important tool in sport medicine and in clinics. Lactic acid is the final product of the anaerobic glycolysis and during intense exercise its concentration increase because of the switch of muscle cells to anaerobic metabolism. Lactic acidosis is found also in all diseases involving inadequate intake of oxygen to tissues (hypoxia), and this is spy of organ failure and dysfunction: acute congestive heart failure, renal or hepatic failure, respiratory failure, severe pulmonary disease, pulmonary edema, severe anemia, diabetes not under control and a number of rare inherited metabolic and mitochondrial diseases (forms of muscular dystrophy, ALS ...). Hyperlactemia is typical of patients with severe sepsis or septic shock, it can be secondary to the anaerobic metabolism due to the hypoperfusion and it has a prognostic value. The symptoms of hypoxia requiring a lactate test are: wheezing, shortness of breath, pallor, sweating, nausea, muscle weakness, abdominal pain, coma. In all these conditions is of fundamental importance to repeat the measurement at intervals to keep under control the conditions of the patient also in response to a therapy.
The determination of lactate is usually performed in blood. However, in the last years the measurement of metabolites in media other than blood is becoming very significant because of the demand of non-invasive analysis. Such measurement are very important to avoid physical and mental stress, risk of infection and the presence of medical staff. Matrices as urine, saliva and sweat are very useful either to control daily parameters in hemophiliacs, neonates and elder patient, either to monitor the training of athletes.
In this work we have developed simple chromatographic methods for determination of lactate in sweat, urine and saliva. Sweat contains a lactate concentration ranging between 1 and 60 mM (10 times higher than lactate concentration in blood, saliva and urine). For sweat samples no particular sample pre-treatment was required. For complex matrices as urine and saliva (lactate concentration ranging between 0.1 and 5 mM) we developed a straightforward derivatization method to guarantee selectivity and sensitivity and to control the matrix effect. The lactate concentration results found using the chromatographic methods were compared with those obtained by a novel, portable lactate analyser® based not on enzymatic reactions, but on a photochemical reaction that occurs *in situ* onto a disposable electrode.

P06 - SCREENING OF CYANOBACTERIAL HEPATOTOXINS IN WATER SAMPLES: OPTIMIZATION OF A COLORIMETRIC PHOSPHATASE INHIBITION METHOD

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Microcystins (MCs) and nodularin are a class of cyclic natural peptide hepatotoxins produced by cyanobacteria such as *Microcystis*, *Oscillatoria*, *Anabaena* and *Nodularia*, usually found in lakes, water reservoirs and recreational facilities. They exert the cytotoxic effects by inhibiting the catalytic activities of serine/threonine protein phosphatase-1 (PP1) and phosphatase-2A (PP2A) disrupting the normal signal transduction pathways. Cyanobacteria and their toxins, especially 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, with overestimation in the toxicity assessment, the value of 1 μg/L would be referred to the sum of the hepatotoxin concentrations present in the sample, considered as equivalents of MC-LR [1]. A promising approach in measuring MCs and nodularin is based on their inhibitory effect of PP2A and PP1 enzymes. The degree of inhibition of these enzymes can be used as a measure of toxin concentration. In this work (part of ACQUASENSE Industria 2015 project), we propose a colorimetric assay in which the activity of protein phospharase-2A is determined by measuring the rate of colour production from the release of yellow *p*-nitrophenol using *p*-nitrophenyl phosphate as the substrate. In the presence of MCs and nodularin enzyme inhibition occurs and consequently the rate of colour production decreases proportionally to the concentration of the toxins. Changes in absorbance at 405 nm are measured by a microtiter plate reader after incubation for 150 minutes in an appropriate microtiter stirrer at 30°C. Preliminary experiments were performed according to previous works reported in the literature, but without satisfactory results [2, 3]. So our attention was focused on the optimization of the experimental conditions such as the "buffer for the enzyme dilution", the PP2A concentration, and the "assay buffer". Although Mn^{2+} is not listed as a component of the assay buffer by the supplier of these PP2A enzyme (Upstate Biotechnology) its presence was proved to be indispensable. Moreover, in order to develop a very sensitive method for the screening test we have optimized the volume of the standard/sample solution to add in the well; a large volume of 125μL per well was chosen in a total volume of 300μL. In these conditions a typical sigmoidal calibration curve was obtained with a detection limit of 0.08 μg/L, a working range between 0.2 and 0.5 μg/L and an IC_{50} value of 0.33 μg/L. Considering these results it will be possible to analyze drinking water directly without a preconcentration step. Experiments in water samples are in progress.

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P07 - IMPROVEMENTS IN THE DETERMINATION OF SULFIDE, CYANIDE AND THIOCYANATE BY CHEMICAL VAPOR GENERATION COUPLED WITH HS-GC-MS

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The use of trialkyloxonium salts has been recently proposed for the determination of anionic species by chemical vapour generation (CVG) coupled with head-space gas chromatography mass spectrometry (HS-GC-MS). In particular the use of aqueous Et_3O^+ BF_4^-reagent is attractive because it is able to generate volatile ethyl derivatives of chloride, bromide, iodide, sulfide, cyanide, thiocyanate, nitrite and nitrate [1]. Fluoride can be also determined by using aqueous Et_3O^+ $FeCl_4^-$ [2] Some anions such as sulfide, cyanide and thiocyanate show detection limits in the range of 200-400 ng/mL, which are more than two orders of magnitude worse than those obtained for the other anions. In the present work is reported a study for the optimization of the reaction conditions with the aims to get significative improvements in the sensitivity of CVG-HS-GC-MS determination of these anions.Mechanistic aspect of CVG of anionic species, at trace level, by aqueous phase alkylation with R_3O^+ salts has not been investigated, but their knowledge is important for the optimization of reaction conditions and for the control of interferences. The first approach is to identify all the possible reactions involved in the generation and in the liquid-vapor phase transfer of the volatile analytical derivative, RX. They can be classified as analytical reactions, competitive reactions and interfering reactions.The optimization of experimental conditions should take into account the experimental parameters which play a role in controlling all the possible reactions above mentioned. The first approach is to consider temperature, time, acidity and amount of reagent as the most critical parameters which play a major role in controlling the analytical reaction system. The choice of chemical additives (buffers, masking agents) represents a critical aspect of this derivatization procedure due to the reactivity of trialkyloxonium salts with other anionic species or ligand/donor species.The optimization of reaction conditions has been performed by experimental design by changing the concentration of buffering species controlling acidity (NaOH and NH_3), the concentration of Et_3O^+,temperature and reaction time. The experiments indicate that a careful optimization could improve sensitivity by several orders of magnitude and confirm the role played by reactions 1-2, 3-6 and 8-9 in the control of the analytical derivatization procedure. All optimization experiments were performed by using a GC-MS system (Agilent 5975c mass spectrometer and 6850 gas-chromatograph equipped with head space autosampler and incubating tool (Combi PAL CTC).Under optimized conditions the detection limits (3*s*) are 0.08, 35 and 1.7 ng/mL for sulfide, cyanide and thiocyanate, respectively, which represent improvement factors of 4×10^3,10, 160 with respect to the previously reported figures [1]. Application to biological samples (thiocyanate and other anions in human saliva and plasma) are reported.

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P08 - A NEW GALACTURONIC ACID BIOSENSOR BASED ON A RECOMBINANT URONATE DEHYDROGENASE ENZYME FROM *PSEUDOMONAS SYRINGAE*

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D-Galacturonic acid is a sugar acid, an oxidized form of D-galactose, that is the main component of pectin, a natural polymer that exists in primary cell walls of terrestrian plants. D-Galacturonic acid as well as other sugar acids such as D-gluconic and D-glucuronic acids are associated with grape infection by *B. cinerea* [1]. They are characteristic of the disease and therefore their presence has been used as an indicator of the degree of infection. None of these sugar acids affects taste or odor of wine, however, D-galacturonic acid may be involved in the browning of white wines, a process of continuous oxidation which can cause loss of aromatic freshness and, in the final stages, the appearance of precipitates of condensed phenolic material in the bottled wine [2]. The determination of D-galacturonic acid is therefore of particular interest in wine production. Food control analyses require robust, sensitive, and selective detection methods. The most commonly used methods such as chromatography and mass spectrometry require expensive instrumentations and skilled technicians. Enzyme biosensors are a good alternative because they incorporate robustness and selectivity to low cost of equipment and easiness of sample preparation [3].
In this work a new biosensor for D-galacturonic acid detection has been assembled by using a carbon screen printed electrode modified by depositing a solution of photocrosslinkable polymer (PVA-SbQ) containing appropriate amounts of uronate dehydrogenase from *Pseudomonas syringae* [4] and diaphorase from *Clostridium kluverii* enzymes. The optimized biosensor showed a good linear range (8.5-43 mg/L), good reproducibility (2.0%, n=6) and also good stability. The proposed biosensor was successively applied for the determination of D-galacturonic acid in different samples of wine.

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P09 - DETERMINATION OF ANTICOAGULANT DRUGS AND THEIR METABOLITES IN ORAL FLUID: STRATEGIES FOR SAMPLE COLLECTION.

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Warfarin is the most common anticoagulant drug prescribed for the treatment of many diseases. It is metabolized by the cytochrome P450 to inactive hydroxylated metabolites and by ketone reductases to warfarin alcohols, which show a little anticoagulant activity. The standardized evaluation of the coagulation time (international normalized ratio, INR), which requires blood sampling, is the primary assay used in monitoring warfarin therapy. New methods alternative to blood tests are needed that would be less invasive, simple to use, implementable in low cost devices, and, if possible, allowing self-monitoring.
Methods for the determination of warfarin and warfarin alcohols in oral fluid and plasma were developed based on HPLC-fluorimetry. Fluorescence detection was performed at 390 nm (excitation wavelength 310 nm). LODs for warfarin and warfarin alcohols were 0.2 and 0.1 ng/mL, respectively, recoveries ranged between 90% and 70%, and intra- and inter-day precisions were <10% (RSD) for all methods.
In order to establish the best oral fluid sampling that provide the highest correlation between the oral fluid and unbound plasmatic concentration of warfarin and warfarin alcohols, a cross-sectional study was performed involving 10 patients undergoing warfarin therapy. Te influence of sampling procedure on the correlations between salivary flow rate, pH and concentration of warfarin and warfarin alcohols was investigated. These results confirmed the importance of pH in regulating the drug transfer from plasma to oral fluid, and indicate that oral fluid may be a clinical tool for therapy monitoring.

P10 - DIFFERENTIAL PROTEOMIC ANALYSIS OF PRIMING-INDUCED SALT TOLERANCE IN DURUM WHEAT

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Durum wheat is the most widely cultivated crop in the Mediterranean basin. Soil salinity is one of the most brutal environmental factors limiting the productivity of crop plants. Seed priming, a seed pre-sowing imbibition treatment, has been demonstrated to be an efficient method to improve seed performance with respect to rate and uniformity of germination, especially under stressful conditions [1]. In particular, seed priming with antioxidant compounds, such as ascorbic acid, seems to be an efficient method to overcome seed germination problems and to improve seedling growth in the field, especially under salinity [2]. In this work, an LC-MS/MS platform for the analysis of metabolic proteins from durum wheat seeds was carried out to characterize proteins that are potentially associated with priming-induced salt stress tolerance in durum wheat. Solubility-based protein fractionation [3] and protein enrichment [4] combined with label-free quantitative shotgun proteomic analysis was conducted using primed and unprimed seeds. The proteome profiles and quantitation results were exploited to examine whether the effects of seed priming could be related to an advance in germination due to the realization of germination-related processes or other particular mechanisms. Toward this goal, we used durum wheat seeds of varying vigor as generated by hydro- and ascorbate- priming treatments.
Results indicated that hydro-priming was accompanied by significant changes of 79 proteins, most of which were involved in proteolysis, protein synthesis, metabolism and disease/defense response. Ascorbate-priming was also accompanied by significant changes of 91 proteins, however they were mainly involved in protein metabolism, antioxidant protection, repair processes and, interestingly, in methionine-related metabolism. This approach could be used to deeper investigate the seed proteome and to find possible biomarkers of priming-induced salt tolerance in durum wheat.

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P11 - EQUILIBRIUM BINDING LANGMUIR ISOTHERMS FOR DIFFERENT BILE ACIDS TO CHOLESTYRAMINE AND COLESEVELAM RESINS

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Cholestyramine and Colesevelam, nonabsorbable, positively charged resins or hydrogels, are the main bile acid (BAs) sequestrants on the market that bind BAs and other hydrophobic anions in the gastrointestinal content. Such binding decreases the flux of bile acids through the ileal enterocytes, resulting in less fibroblast growth factor 19 (FGF19) being formed and released resulting in an indirect up-regulation of the low density lipoprotein (LDL) receptors of the hepatocyte, decreasing plasma cholesterol levels. A better understanding of the interaction between these sequestrants and the BAs is needed to identify the physico-chemical factors that are involved and responsible for the binding and its BAs selectivity. An equilibrium binding experimental model was developed to determine and quantify in term of capacity and affinity the interactions between adsorbate and adsorbent. A fixed amount of dry BA sorbent (0.003g), i.e. cholestyramine or and colesevelam, was incubated for 24h at 37°C under controlled stirring, with sodium salt of chenodeoxycholic acid (CDCA), its taurine (CDC-tau) and glycine (CDC-gly) conjugates covering the range of 0.3-1.5 mM in BES 0.05M pH=7,2 buffer. Bile acid concentration at equilibrium was determined by HPLC-ES-MS/MS. The maximum binding capacity q_m (mmol/g) of each sequestrant and the affinity of the sorbent for BA b (l/mmol) were calculated according to the Langmuir isotherm equation. Since one of the assumptions of the Langmuir isotherm provides that the adsorbate-adsorbate interaction is considered negligible compared to the interactions of adsorbate-adsorbent, it was decided to work in a range of concentrations below the critical micelle concentration. For all the studied BA molecules, the maximum binding capacity was slightly greater for cholestyramine (2.5-3.1 mmol/g) than colesevelam (1.5-1.9 mmol/g) while the affinity for colesevelam was much greater than that of cholestyramine, respectively 11.9 times for CDCA, 5.3 times for CDC-gly and 4.1 times for CDC-tau.

These data suggest that the BAs structure play an important role in the modulating resin binding and therefore additional BA structure-binding studies are required to design new BA sequestrant more efficient and selective.

P12 - SHOTGUN PROTEOMICS CHARACTERIZATION OF SERUM PROTEINS ADSORBED ONTO PEG-MODIFIED LIPOSOME NANOPARTICLES

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Cationic liposomes are promising non-viral nanovector systems for gene therapy. However, when they are exposed to biological media they interact with proteins, which adsorb on their surface forming a “protein corona”. These interactions have an essential role for nanovectors biodistribution and gene therapy in in-vivo applications because they strongly affect the transfection efficiency [1]. As a consequence, these phenomena become one major issue with liposome application in drug delivery, critical for in-vivo distribution and nanoparticle removal from the body. In order to tackle this problem, liposome surfaces were derivatized with polyethylene glycol (PEG) molecules to reduce protein adsorption onto liposome nanoparticles, thus extending blood-circulation time while reducing mononuclear phagocyte system uptake [2]. In this work three different pegylated liposome formulations were compared to the non-pegylated one in order to characterize their protein corona when exposed to a biological medium, serum. The three pegylated liposomes were functionalized with different PEG chain length, 1000, 2000 and 5000, in order to evaluate the effect on protein adsorption. The four liposome types were incubated for one hour with human serum and the nanoparticle-protein complexes were isolated by centrifugation. Recovered proteins were denatured and trypsin digested, and the resulting peptides were separated by reverse phase nanoHPLC and directly injected into a LTQ Orbitrap XL mass spectrometer for MS/MS analysis. Data collected were processed by Proteome Discoverer in order to retrieve protein identifications for the different samples. The resulting protein profiles were very similar for all the liposome systems, indicating that they basically bind the same protein classes, including fibrinogen, complement system proteins and immunoglobulins, which are responsible for liposome removal from the bloodstream. However, binding occurs with different ratios and results indicate a strong correlation between PEG chain length and the amount of proteins which adsorb on the liposome surface, with greater amounts for shorter chain lengths.

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P13 - THE TIME EVOLUTION OF NANOPARTICLE-PROTEIN CORONA IN HUMAN PLASMA: A PROTEOMIC APPROACH.

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Over the past few decades, there has been extensive interest in developing biodegradable nanoparticles (NPs) as effective devices in view of their applications in the delivery of drugs, proteins, peptides and nucleic acids. Among existing NPs, lipid NPs exhibit unique advantages, which include increased stability of drugs, ability to protect drugs from degradation, target the drug to the site of action and controlled release properties. When lipid NPs enter a biological fluid, several proteins compete for binding to the NP surface [1]. The most relevant implication is that the identity of the bare NP is rapidly lost, and the biological behavior is dominated by the layer of adsorbed proteins, the so-called “protein corona” whose composition, time evolution and fate in vivo are dictated by the physical–chemical properties of the NP itself. Recently, it has been shown that the corona composition changes with time due to continuous protein binding and unbinding events. [2]. In this study we investigate the time evolution of the protein corona associated with lipid nanoparticles whose lipid envelope is a binary mixture made of the cationic lipid 3β-[N-(N´,N´-dimethylaminoethane)-carbamoyl] (DC-Chol) and the zwitterionic lipid dioleoylphosphatidylethanolamine (DOPE). Exposing DC-Chol–DOPE lipid vesicles to human plasma, a clear evolution of the associated protein corona over time was observed; incubation time was ranged from 1 to 60 min. A modern shotgun proteomics approach was employed to compare the protein profile of protein corona after 1min, 30 min and 60 min of incubation. In particular an analytical platform was drawn up which involved the use of solubility-based protein fractionation followed by nano-liquid chromatography-tandem mass spectrometry analysis combined with label-free quantitation. This proteomic study revealed apolipoproteins as the most abundant component, which suggests an improved biocompatibility and indicates novel opportunities for targeted drug delivery.

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P14 - COMPUTATIONAL DESIGN AND SELECTION OF BIOMIMETIC RECEPTORS FOR PESTICIDES SELECTIVE EXTRACTION

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Organophosphorus compounds have come into widespread use in agriculture, since they show low environmental persistence; nevertheless, they exert a high acute toxicity. The principal effect of these compounds is the inhibition of the enzyme acetylcholinesterase (AChE), which is essential for terminating the action of the neurotransmitter acetylcholine (ACh). In pesticides detection, sample preparation is a critical step and is a key factor in determining the success of analysis. Solid phase extraction (SPE) is commonly used for the clean-up of complex samples. Traditional SPE sorbents range from reverse phases to ion exchange and polymeric materials [1-3]. These materials are not selective and can result in the co-elution of interfering compounds with similar polarity leading to matrix effect, that can affect the reliability of the analytical method. For these reasons, three different hexapeptides were computationally designed and tested as selective SPE sorbent for chloropyriphos e pirimiphos-methyl. The approach chosen in this work relies on the design and development of artificial oligopeptides based on binding site of acetylcholinerase (AChE) [4]. The hexapeptide-pesticides complex binding scores were compared with the SPE results. Before the SPE procedure set-up, detection conditions were optimized with standard solutions. The extraction procedure for SPE was also optimized considering volume loading, pH effect, washing and elution conditions and interferences. The resulting data were presented and discussed.

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P15 - TOWARDS THE INTEGRATION OF REAL TIME PCR IN LAB ON CHIP DEVICES

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Great research efforts are being devoted to the development of miniaturized self-standing analytical tools for the molecular diagnosis of infectious diseases in a point-of-care (POC) setting. Real-time PCR is nowadays the gold standard for rapid and ultrasensitive quantitative detection of specific DNA or RNA sequences. Nevertheless, such technique is not suitable for POC, requiring dedicated and expensive laboratory instrumentation and specialized personnel.
In this work, we describe our route towards PCR-based quantitative DNA detection in a lab-on-chip format. Firstly, isothermal DNA amplification systems, either exploiting the helicase-dependent method [1] or the loop-mediated isothermal amplification (LAMP) [2], are being evaluated to facilitate on-chip target amplification. In addition, quantification of the amplification product is performed by the Bioluminescent Assay in Real-Time (BART) system, based on the detection of the pyrophosphate released by DNA polymerase through its conversion to ATP by means of ATP sulphurylase, followed by ATP detection using the luciferase-luciferin bioluminescent system [3].
Preliminary results showed the possibility to achieve low limits of detection for pyrophosphate, down to 0.7 pmol μL^{-1}, and the ability of the helicase-dependent isothermal amplification reaction to specifically amplify target DNA sequences from human Parvovirus B19, down to 10^2 copies per reaction.

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P16 - ON-CHIP CHEMILUMINESCENCE DETECTION OF ENZYME LABELS BY MEANS OF INTEGRATED AMORPHOUS SILICON PHOTODIODES

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During the last decades microfluidic-based chips have emerged as powerful analytical tools for accurate and rapid analyses in the clinical diagnostics, agrofood and environmental fields. Nevertheless, their commercial application in point-of-need and point-of-care (POC) settings is still hampered, in most cases, by the absence of fully integrated devices, in which all the system components necessary to perform the entire analytical process (sample preparation, analysis and detection) are included in a single low-cost microfluidic platform. Among optical detection–based miniaturized systems, chemiluminescence (CL) detection of enzyme labels has been shown to provide high assay detectability and specificity and to be well suited for miniaturization [1]. Nevertheless, external detection systems are generally employed (cooled CCD or photomultiplier tubes), thus partially compromising the system portability.
Herein, we describe a microfluidic-based analytical device integrating hydrogenated amorphous silicon (a-Si:H) photodiodes for on-chip detection of CL signals and the evaluation of its analytical performance, as compared with a state-of-the-art commercial ultrasensitive cooled CCD-based acquisition system. The photosensor is a p-i-n structure deposited by Plasma Enhanced Chemical Vapour Deposition on a glass substrate covered with a transparent conductive oxide. An array of PDMS microwells, or a PDMS-based microfluidic network (depending on the application) has been fabricated and bonded on the glass substrate. The detectability of different enzyme labels commonly employed in bioanalytical methods was found to be comparable with that obtained with CCD-based laboratory equipment (e.g., limits of detection for horseradish peroxidase were 70 and 30 fg μL^{-1}, respectively) and applicability on a model immunoassay was shown.

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P17 - EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE ACTION OF CHLOROSULPHONATED PARAFFINS ON COLLAGEN MATRICES

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Elastic properties, mechanical strength, thermal stability and resistance to external agents are some of the characteristics features of collagen-based materials which are highly investigated because of their effective applications in industrial tanning. Indeed, collagen matrices are the main target in leather tanning, where different types of treatments are required to obtain the desired end products. The addition of lubricants or fatliquors during the final phase of the process is necessary to overcome the negative stiffening effects caused by the previous phases and impart softness, smoothness and flexibility to the tanned materials. In this work the binding of chlorosulphonated paraffins (SCPs) to collagen triple helices is studied by means of Fourier Transform Infrared Spectroscopy (FTIR) and classical molecular dynamics simulations (MDs). The study has been focused on disclosing the cooperative effort of all the molecules (collagen triple helices + tanning agents) to form various aggregates with specific characteristics rather than on the resulting mechanistic properties of the organized material as a whole. Thus, explicit molecule-to-molecule interactions and supramolecular arrangements have been analyzed in detail. The experimental technique and the spectral curve-fitting procedures have shown the capability of characterizing the degree of secondary structure and evidence its changes in collagen samples. These were associated mainly to the action of SCPs to form effective and durable cross-links. The type of structural deformations appeared to be connected to the number of cross-links: higher cross-linked complexes were subject to global reorganizations, whereas lower cross-linked pairing rearranged more independently.
In agreement with the experimental observations, the modeling studies revealed preferential interactions between SCPs and collagen which involved the side chains of positively charged amino acids, namely Arg and Lys, and of those amino acids containing an amine group, namely Asn, Gln, suggesting the formation of covalent thionylamine bonds. However, strong hydrogen bonding interactions were also engaged between the SCP oxygens and the hydroxyl groups of Hyp, Ser and Thr. These results could be a good starting point to design new eco-friendly tanning agents to be used effectively in synthetic fatliquoring.

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P18 - PROTON COUPLED ELECTRON TRANSFER IN ADENOSINE SELF-AGGREGATES

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Proton coupled electron transfer (PCET) is of outstanding importance in biochemistry, especially in the fields of photosynthesis and oxidative DNA damages.[1,2] Herein, as a first step toward the study of the adenosine:thymidine H-bonded complex, we report spectroelectrochemical measurements of the UV-vis and IR absorption spectra of oxidized adenosine (Ado) in dichloromethane, which unequivocally demonstrate the occurrence of a PCET in Ado oxidation [3, 4].
Spectroelectrochemical measurements indicate that in CH_2Cl_2 Ado oxidation at the electrode induce self-association, followed by PT from the exocyclic amine group of oxidized Ado to the N1 and in a lesser extent to N7 nitrogens of the neutral Ado partner. Understanding whether electron transfer can be coupled to PT in DNA is of outstanding importance, because PT processes can both affect nucleobase oxidation potential and inhibit long range hole transfer along DNA single strand or duplex. Spectroelectrochemistry appears to be a very powerful and promising tool for investigating PCET processes and more generally the reaction mechanisms of electrolyzed species.[5,6,7].

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P19 - STACKING INTERACTIONS BETWEEN ADENINES IN DNA OLIGONUCLEOTIDES

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Stacking interactions play a major role in DNA oxidation, because they finely modulate the redox potential of DNA nucleobases, in a way which depends on the primary and higher order structures. [1] Indeed, there is experimental evidence that sequences of adjacent guanines (G), the nucleobase with the lowest oxidation potential, are the most easily oxidizable sites in DNA, GGG sequences being still more reactive than GG ones.[2-4]. The effects of stacking interactions on the oxidation potentials of single strand oligonucleotides containing up to four consecutive adenines, alternated with thymines and cytosines in different sequences and ratios, have been determined by means of differential pulse voltammetry. [5] Here, we present a series of voltammetric measurements -a well suited experimental tool for detecting the effects of inter-base interactions on the oxidation potentials of the nucleobases- [6-7] of oligonucleotides containing adenines in different sequences and ratios, which in physiological conditions exhibit multiple signals, characteristic of π stacked molecular systems, which allow a quantitative determination of the strengths of stacking interactions between two stacked adenine units.
We have shown that voltammetry is a powerful method to quantify the strength of stacking interactions in oligonucleotides, providing the necessary physical quantities for understanding the complex landscape of electronic states which controls long range hole transfer.

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P20 - DNA LABELLED NANOPARTICLES FOR IMPROVED SURFACE PLASMON RESONANCE IMAGING

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DNA sensing based on surface plasmon resonance (SPR) was often coupled to metal noble nanoparticles with the final aim to improve analytical performances in terms of detection limits and sensitivity [1-3].
The improvement of analytical performances of a DNA sensor based on SPR is a high priority goal in advances devices, mostly in clinical and diagnostics applications.
In this study the effect of coupling between Surface Plasmons (SPs) and electric field of Localized Surface Plasmons (LSPs) of metal noble nanoparticles was studied for the increase of SPR signal in molecular buildings based on DNA and nanoparticles.
A sandwich-like assay was though in a logical way in order to test the performances of the two different synthetized NPs: i.e silver triangular nanoplates (with plasmons) and silica nanospheres (plasmon free).
In particular nanoparticles were covalently bound to DNA probes and analytical SPR signals of hybridization were compared to assess the influence of nanoparticles LSPs on SPR sensitivity. Reflectivity curves and digital image of molecular buildings were also recorded.
As result silver nanoplates provided a SPRi signal enhancements respect to silica nanoparticles (about 160%) due to the change of resonance properties and resulting in improved analytical features.

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P21 - DETERMINATION OF SHIKIMIC, JASMONIC AND SALYCILIC ACIDS IN WILD AND OGM NICOTIANA LANGSDORFII PLANTS EXPOSED TO CHEMICAL AND WATER STRESSES

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The metabolic diversity in plants represents a reservoir of diverse functions; when the environment is adverse and plant growth is affected, metabolism is profoundly involved in signaling, physiological regulation, and defense responses. At the same time abiotic stresses affect the biosynthesis, concentration and storage of primary and secondary metabolites [3,4]. The activation and regulation of the complex system of stress response rely on the kind and duration of stress and to the plant genotype and developmental stage. Changes in the genetic profile of a plant can significantly affect the hormonal pattern and the physiological response to abiotic stresses [1]. The plant response results from multiple phytohormones activity; as a consequence, interest has addressed to multiple phytohormones analysis [2]. In order to verify the different metabolic response to chemical (Cr and Cd exposition) and hydric stresses, the genes rolC and GR rat receptor were introduced in Nicotiana Langsdorfii plants. An HPLC/ESI(-) MS/MS method was developed to simultaneously quantify Shikimic, Jasmonic and Salycilic acid, phytohormones involved in plants' development and stress response . The cromatographical method allows the separation of these compounds in 8 minutes by using a RP-C18 column, eluted with Acetic acid 0.01% and Methanol. Labeled internal standards were used to quantify the phytohormones by isotopic dilution and the results were corrected by evaluating instrumental response factor. The method was validated evaluating precision, accuracy and recovery. Matrix effects were also considered. The method was applied to a few samples of wild and OGM Nicotiana Langsdorfii to assess the variation of the metabolites profile in different stresses conditions.

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P22 - MEASUREMENTS OF VOLATILE ORGANIC COMPOUNDS IN INDOOR AIR OF FLORENTINE MUSEUMS

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Indoor air pollution in museums due to volatile organic compounds (VOCs) is of particular importance in conservation of cultural heritage. On the other hand, it is essential to provide a healthy indoor climate for museum staff and visitors; moreover cultural assets have to be protected against deterioration. In addition to chemical substances generated by human outdoor activities (mainly traffic or industrial activities), also visitors, building materials and exhibits themselves, can be sources of VOCs. Some of them may have a potential hazardous impact on human health and can accelerate the degradation of some classes of materials constituting the exposed masterpieces. The aim of the research was to investigate the VOCs distribution in indoor museum environment in order to qualify and quantify the main compounds and determine their possible sources. An active air-sampling was carried out at four locations of Natural History Museum of the University of Florence (sections of anthropology and ethnology, geology and paleontology, mineralogy and lithology, zoology “La Specola”), in exhibition rooms and inside the showcases to evaluate the current situation at museum sites. VOCs were trapped in stainless-steel desorption tubes filled with Tenax GR; samples were thermally desorbed and analyzed by GC-MS. The results showed that most of the detected compounds are mainly related to traffic pollution, presence of visitors and showcase materials . In particular, were evidenced the presence of compounds potentially dangerous for works of art, such as naphthalene and 1,4-dichlorobenzene. Concentration of siloxanes and terpenes were also determined in some samples.

P23 - THE ROLE OF ENVIRONMENTAL POLLUTANTS ON THE DEGRADATION OF PAINT VARNISHES IN MUSEUM AND MICROCLIMATE FRAMES

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Understanding the degrading action of indoor environmental pollutants is fundamental in order to evaluate the conservation conditions of paintings stored in museums in general and microclimate frames in particular. Varnishes represent the first barrier that a painting exposes to the external evnironment. The EU PROPAINT e FP7 MEMORI focussed on the impact of inorganic (NO_2 and O_3) and organic pollutants (acetic and formic acid) on paint varnishes made of commonly used natural and synthetic resins. Mastic and dammar resins, Laropal A81 and Regalrez 1094 were used to prepare model paint varnishes, using both stainless steel and glass as support. These model systems were artificially aged by using varying doses of pollutants and analysed by mass spectrometric (GC-MS , ESI-MS, MALDI-TOF and SIMS) and physicochemical techniques (μTA, DMA). Model varnishes were analysed after artificial ageing and periodically, for a year, in order to understand the damage due to the exposure to the investigated pollutants, and to evaluate as this evolves with time. Data indicate that both acetic and formic acid show a degrading effect, comparable to that of inorganic pollutants, which probably involves the catalysis of oxidising and cross linking reactions naturally taking places in these resins as an effect of natural ageing. The study also revealed that the degradation of dammar resin under exposure to acetic and formic acid is slowed down by a layer of Regalrez 1094. This indicates that a varnish made up of a layer of dammar and one of Regalrez 1094 is potentially better performing from the optical point of view and shows a slower degradation rate than a varnish made of a simple natural resin. The research performed demonstrates that environmental pollutants, including organic acids, contribute to the degradation of paint varnishes, and thus monitoring the concentration of organic acids is fundamental in order to ensure a good air quality and thus a correct conservation of varnished paintings [1].
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P24 - MULTIVARIATE DATA ANALYSIS APPLIED TO THE STUDY OF CORROSION

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The artistic and architectural heritage exposed to the environment is constantly subjected to many risk factors, natural and anthropogenic, which may cause degradation, accelerate the corrosion processes or prevent their proper maintenance. Metals and alloys constitute a class of materials that has always played a key role in several applications, thanks to their peculiar aesthetic and mechanical features.
Unfortunately, as a consequence of environmental exposure, these materials could release a certain quantity of alloying metals that could disperse in surrounding areas (soil and water) or accumulate near the structures, thus constituting a potential hazard to the environment and to organisms.
Among the several factors that can influence this process, the action of atmospheric variables and especially the presence of several air pollutants constitute the main corrosion agents.
In this scenario, chemometrics and in particular data exploration techniques, became a fundamental tool for better examine the behavior of these materials after environmental exposure, which implies the involvement of many variables.
The aim of this work was to exploit multivariate analysis to integrate environmental variables (temperature, wind directions and intensities, rain composition, main airborne pollutants) with information related to degradation processes of alloys, such as steels (in particular Cor-Ten®, a low-alloyed steel with the peculiar ability to self-protect from atmospheric corrosion) and bronzes.

P25 - NEW METHODOLOGIES FOR CLEANING TREATMENT OF PAPER ARTWORKS: SOME CASE STUDIES

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Wet cleaning of ancient papers is one of the most used conservation treatments able to improve the optical qualities of a graphic work and remove dust and organic substances resulting from cellulose degradation. Nevertheless, washing treatment can induce swelling with deformation of paper material after drying and can be dangerous for water sensitive inks and pigments.
In order to minimize the disadvantages caused by the use of "free" water, an alternative washing method based on the use of a rigid hydrogels has been developed. Due to its high retention power and viscoelastic properties, the water penetration into paper sheets is significantly reduced.
We present the results obtained applying a Gellan gel as cleaning agent on paper samples belonging to different centuries (form XVI to XIX century) [1]. Moreover we have performed studies for using Gellan gel as carrier of additional cleaning agents such as α-amylase enzymes or polymeric surfactants to remove respectively starch paste or hydrophobic materials from paper samples. To assess the effectiveness and safety of the proposed cleaning methods, several techniques, such as HPLC, FTIR, scanning electron microscopy, UV-Vis microscopy and pH measurements have been employed. In addition, to monitor the health state of paper samples and/or cleaning process in real time, we are developing specific electrochemical biosensors able to detect the presence of a specific degradation product [2]. The aim is to obtain an efficient cleaning method coupled with a biosensor indicating the end of the process. In our preliminary studies we have chosen to detect glucose as final target the cellulose degradation. The combination of all results obtained highlights and confirms the efficacy and selectivity of the proposed cleaning method.

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P26 - NON-DESTRUCTIVE IDENTIFICATION OF CONSERVATION TREATMENTS OF THE DEAD SEA SCROLLS BY USING DART-MS

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In this study, we developed a new non-invasive method for the identification of unknown interventions of parchment by using DART-MS and statistics.
Many conservation techniques used in the past can result in irreversible alteration of an artifact when applied and in addition, because of its animal origin, parchment can respond to conservation treatments in unpredictable ways. The conservator's approach to the treatment of parchment must be extremely cautious and due to the simplicity and no sample preparation requirement, the proposed analytical tool could help them in the challenging analysis of unknown conservation treatments in cultural heritage.
Castor oil and glycerol parchment conservation treatments were investigated using the DART ionization source at room temperature in order to do not cause any damage to parchment samples: this is very important while working with any cultural heritage and even more with the Dead Sea Scrolls which are very fragile and precious.
The method was able to identify both conservation treatments: FS-LDA performed on principal components revealed to be a robust tool that could be employed for the classification of unknown conservation treatment, over all in presence of samples with similar mass spectrum profiles.

P27 - STATISTICAL ANALYSIS OF AMINO ACID FINGERPRINT TO CHARACTERIZE PROTEIN BINDERS IN WORKS OF ART

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Historically, the diagnostics of proteins in the field of conservation science has always been complex due to several factors, such as the protein structure, the degradation due to the effects of aging; the presence of interference effects of pigments and the smallest amount available. Usually the techniques employed for the identification and the determination of protein material were chromatographic techniques, such as GC/MS and HPLC. Recently, we reported the amino acid analysis by AccQ•Tag Ultra UPLC (Ultra Performance Liquid Chromatography) of standard protein materials (ovalbumin, whole egg, egg white) and model specimens, compared to Dot-ELISAs [1]. In this work we propose the UPLC-based amino acid analysis as diagnostics technique for not pre-treated or submitted to extraction processes model and real samples, showing that good results can be achieved with very scarce sample manipulation and great advantage. We perform the amino acids analysis by the AccQ•Tag™ Ultra UPLC method first to the standard protein samples and then to model and real samples. In particular, after protein hydrolysis (24h, 114°C, 6M HCl), the samples were derivatised by 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate (AQC) and separated /detected with UPLC instrument.
The results obtained confirm the reliability of the data achieved and demonstrate that the AccQ•Tag™ Ultra UPLC method could be a powerful technique to be applied to the field of protein binders diagnostics for paintings conservation. The acquired data were processed statistically by means of Multivariate Analysis. Principal Components Analysis (PCA) was employed mainly to screening data in search for the compounds present in the mixture analysed. The multiple linear regression model was used to find the main compounds present in the mixture under investigation, starting characterizing which profiles have to be taken into account to explain a given chromatographic pattern. The linear regression model and error in the variables methodology has been extensively used in the study to build reference patterns of basic compounds. Finally from the analysis of compounds we have realised a reference table of compounds and using these we have expressed all estimates in terms of ovalbumin, casein and glue units of reference values.

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P28 - INTEGRATED MASS SPECTROMETRY APPROACH FOR THE CHEMICAL CHARACTERIZATION OF ORIGINAL PAINT TUBES USED BY EDVARD MUNCH

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A multi-analytical approach based on different mass spectrometric analytical techniques was used for the analysis of the content of seven paint tubes from the study of Edvard Munch (1863 - 1944), Norway's most famous painter and front figure in modernism.
The Munch Museum in Oslo and the Museum of Cultural History of the University of Oslo have established a project to investigate the tubes and catalogue them. In the framework of this project, we used GC/MS and HPLC-ESI-Q-ToF to study the composition of the organic binding media. We aimed at improving the knowledge of the paint materials used by artists in the late nineteenth century and the first half of the twentieth century, in correspondence to the introduction and the diffusion of commercial oil paint tubes.In particular, GC/MS analysis after hydrolysis, extraction and silylation allowed us to identify the fatty acid profile of the paint material and to study the molecular changes associated to curing and ageing, such us the oxidation of double bonds and the formation of dicarboxylic acids.
(RP)HPLC-ESI-Q-ToF using positive ionization mode and tandem mass spectrometry was used to determine the distribution of triglycerides (TAGs). The obtained data will be exploited to better understand Edvard Munch's painting technique. They will also contribute to address dating, authenticity and conservation issues by comparison with the results of analysis of paintings.

P29 - LIQUID CHROMATOGRAPHY-HIGH RESOLUTION MASS SPECTROMETRY-BASED METHOD TOWARDS THE COMPREHENSIVE ANALYSIS OF MIGRATION OF PRIMARY AROMATIC AMINES FROM FOOD PACKAGING

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Primary aromatic amines (PAAs), which are toxic compounds and suspected human carcinogens, can migrate from plastic multilayer laminated films and colored food contact materials into foods: they can be found as residuals from incomplete reactions as by-products or degradation products. To protect consumer health, EU legislation has established that plastic materials and articles shall not release PAAs (detection threshold: 0.01 mg/kg of food or food simulant) [1]. Currently the determination of PAAs is based on a colorimetric measurement [2] or on more accurate and selective targeted LC-MS/MS approaches [3]. Taking into account the advantage of specificity of accurate mass and the intrinsic limitation of multiple reaction monitoring acquisition mode, that does not permit retrospective screening analysis, a LC-Orbitrap-full scan-HRMS method was devised and validated for the determination of migration levels of 22 PAAs from FCM. Recently, our research group successfully proposed DESI-Orbitrap-HRMS methods in the field of food safety [4]. The direct injection of the simulant (acetic acid 3%, *w/v*) after the migration, without any pre-treatment step, makes the devised method of great value for rapid screening analysis of a large number of amines. A very fast and efficient separation (<11 min) of PAAs was achieved. Good results in terms of detection limits (0.06-0.7 µg/kg), dynamic linear ranges (2-4 orders of magnitude), intra- and inter-day repeatability (RSDs < 17%) and recovery (70±1-131±5%) were obtained, thus proving method reliability for the quantification of the PAAs at trace levels. Finally, the method was successfully applied to a range of different kinds of FCM, detecting negligible PAAs residual levels in some samples.

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P30 - CALIBRATION AND PERFORMANCE EVALUATION OF A PULSED REPETITIVE INTERFACE FOR ONLINE TGA-GC-MS ANALYSIS; APPLICATION TO THE CHARACTERISATION OF COMPLEX LDH SAMPLES.

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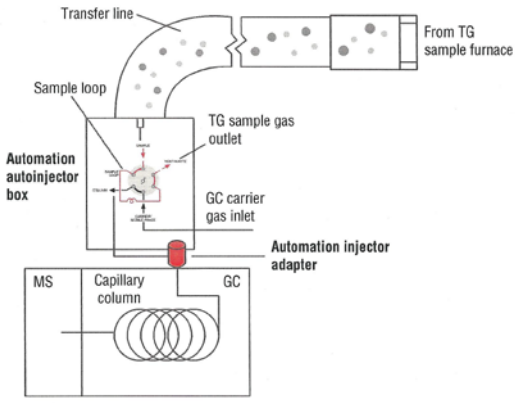
Layered double hydroxides (LDH) are versatile materials used for intercalating bioactive molecules, both in pharmaceutical and cosmetic fields, with the purpose of protecting them from degradation, enhancing their water solubility to increase bioavailability, and/or obtaining modified release properties. In those fields the comprehension of the mechanisms involved into de-intercalation, ion exchange and absorption of contaminants, mainly carbonate anions are of paramount importance, but the usually used TGA and DTA analyses does not permit a clear attribution of the weight losses at the various temperatures.
The use of TGA-GC-MS allowed distinguishing and quantifying intercalated and surface adsorbed organic molecules, confirming the presence and amount of carbonate and separating the different types and strength of adsorption, in relation with the temperature of elimination. XRPD demonstrated that the presence of carbonate is able to drive the intercalation of organic into LDH, since CO_3 contaminated samples tend to assume d-spacing roughly multiple of LDH-CO_3 d-spacing.
The evolved gas from TGA was transferred to the GC-MS using an automatic interface (Automation, Milan, Italy) consisting of three components: a heated transfer-line (HTL1) from TGA to an automatic gas sampling system (autoinjector), an autoinjector (AI) equipped by a switch valve and a prefixed volume loop and a second heated transfer line (HTL2) from the AI to the GC-MS injector port. The automatic AI controls the repetitive pulsed transfer of known amounts of the evolved gas, with the desired frequency, in the injector of the GC-MS system.
System performance was evaluated through measuring the level of repeatability under different operation conditions.



P31 - APPROACHES TO IMPRINTED THIN LAYERS FOR CAPILLARY ELECTROCHROMATOGRAPHY

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Recent trends in molecular imprinting technology are focused on the development of innovative approaches for direct synthesis of polymers with controlled morphology. Most of them involve the polymerization of imprinted support within the confines of the micrometric capillary columns in the form of pseudo-stationary phases, monolithic materials or thin layer grafted onto the capillary inner surface.
We compared different surface initiation techniques in order to obtain imprinted thin layers prepared in very small devices as capillary columns, with well-defined thickness and reproducibility, and attractive molecular recognition properties. Three different radical initiators were taken into consideration: 4,4'-azobis-(4-cyanovaleric acid), S-benzyl-S-(carboxyethyl)-trithiocarbonate and propyl-N,N-diethyldithiocarbamate. The inner silica surface of the capillaries was chemically modified by covalently grafting the initiators, the capillaries were filled with polymerization mixture consisted of template, functional monomer, cross-linker and porogenic solvent, and thermal or photo-polymerization was performed. Finally, the molecular recognition properties of the imprinted capillaries were tested by capillary electrochromatography.
Two different polymerization mixtures already reported in literature were used to graft the capillaries. One used 2,4,5-trichlorophenoxyacetic acid in a polar polymerization mixture to achieve binding site able to interact mainly with target ligands through hydrophobic interactions. The other was a polymerization mixture based on a hydrophobic solvent and warfarin as template, with recognition properties characterized by hydrophilic interactions. The molecular recognition properties of the imprinted capillaries were found comparable with those observed in bulk format, but they were related not only to the composition of the polymerization mixture but also to the reactivity of the radical initiator considered.
The experimental results show that only a careful choice of the initiation system can assure the successfulness of the imprinting process.

P32 - VARIATIONS OF THE CONTENT OF PHENOLIC ACIDS IN DURUM WHEAT AS A FUNCTION OF GENOTYPE AND ENVIRONMENT

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Increasing evidence from clinical and epidemiological studies suggests that the regular consumption of whole grain and whole-grain derivatives might reduce the risk of developing chronic illnesses such as cardiovascular diseases, type-2 diabetes, and certain types of cancer. These health benefits have been partly attributed to the occurrence in wheat, as well as in other cereals of phytochemicals with antioxidant activity, which include phenolic acids (PAs) belonging to hydroxycinnamic acids and hydroxybenzoic acids derivatives, such as ferulic, p-coumaric, p-hydroxibenzoic, vanillic and siringic acids. The content of these compounds may have a wide range of variability and their occurrence has been related to the health-promoting effects of whole grains as regards the antioxidant activity. In addition, with the increasing popularity of functional foods, it is crucial to understand the distribution of phenolic compounds in different milling extractions which may have important implications in ensuring their health benefits.
We report the results of a study carried out to evaluate the impact of growing environmental and different genotypes of durum wheat, cultivated in different regions, on the total antioxidant capacity (TAC) and on the occurrence and content of phenolic acids as soluble free, soluble conjugated and insoluble bound acids. The phenolic acids (free, conjugated and bound forms) were extracted following a method developed by Li et al (1) with some modifications and determined by a RP-HPLC method developed in our laboratory. TAC levels were determined following the direct method described by Serpen et al (2), using ABTS radical and expressing data as millimol Trolox equivalent antioxidant capacity per kg (mmol TEAC/kg).

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P33 - HIGH THROUGHPUT ULTRA-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY TRACE ANALYSIS OF PERFLUORINATED COMPOUNDS IN MILK

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Perfluorinated compounds (PFCs), also known as perfluorinated alkylated substances (PFAS), are anthropogenic chemicals widely applied in consumer and industrial products. Due to their unique properties, they are highly stable and extremely persistent in the environment (and in biological samples) with unique profiles of distribution in the body and potential bioaccumulation [1-2]. Because of their adverse effects on human health even at low concentrations [3], these chemicals have received great attention in recent years. Despite this, nowadays there are still few data regarding human exposure to PFAS from food.
This study describes a new, sensitive and easy liquid chromatography/electrospray-tandem mass spectrometric (LC/ESI-MS/MS) method for the determination of 12 PFCs in cow milk. Milk samples were extracted with acetone and cleaned-up by a graphitized carbon black [4] solid-phase extraction cartridge, optimizing the entire procedure by using a screening experimental design. LC/ESI-MS/MS was performed in negative ion mode using multiple reaction monitoring mode. The performance of the method was evaluated using the optimized conditions in terms of matrix effects, range of linearity, accuracy, and repeatability. For all compounds, linearity in matrix was observed in the range LOQ-10 ng injected compound, and coefficients of determination R^2 ranged from 0.9982 to 0.9999. The recoveries were in the range of 91-105%, with relative standard deviations below 6% and method determination limit, based on signal-to-noise ratio of 3, ranged from 0.5 to 5 ng L^{-1}.
The developed method was used to determine the concentration of PFCs in 15 retail milk samples. None of these compounds were detected in the analyzed cow milk samples.

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P34 - FUNCTIONALIZATION OF MESOPOROUS SILICA BY A CAGE-TYPE ANION RECEPTOR (L-MS): BEHIND THE DEVELOPMENT OF A CHLORIDE SENSOR.

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Measurements of chloride concentration are important in a range of applications, i.e. the detection of chloride infiltration into reinforced concrete and the monitoring of active chlorine concentrations in natural and drinking water [1]. Therefore there is an interest in methods for cheap and sensitive monitoring the anion concentration. As well, in many biological fields, chloride-sensors are still largely demanded, since chloride ions are involved in a number of cellular processes such as control of cell volume and pH [2] and new methods are continuously proposed.
It is recognized that the dicopper(II) complex of the bistren (tren = tris(2-aminoethyl)amine) cage **L** shows the unique property to include one chloride ion, in a slightly acidic solution, to give the stable ternary complex $[Cu^{II}_2(L)Cl]^{3+}$, displaying a bright and intense yellow colour [3].
On the basis of these evidences, we decided to anchor the bistren cage **L** to the mesoporous silica MCM-41, with the aim of developing a colorimetric sensor for chloride ions. Recently, we adopted this strategy [4, 5] and two sensors, respectively for anionic radionuclides (ReO_4^- and TcO_4^-) and for Fe(III), were successfully developed.
In the present work, the synthetic pathway, applied to functionalize the silica matrix with the cage-type chloride receptor L (L-MS), is analogous to the scheme previously adopted for the developing of the anion radionuclides sensor [4]. The synthesis is optimized, according to experimental design strategy.
The knowledge of the sorption equilibria of an analyte on the solid phase is necessary to apply the polymer as an extractant and as a sensor; so a wide study on the sorbing properties of the developed solid phases is undertaken.
Finally, the application of the L-MS as colorimetric sensor for Cl^- determination is proposed.

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P35 - CORE SHELL STATIONARY PHASES FOR A NOVEL SEPARATION OF TRIGLYCERIDES IN PLANT OILS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH ELECTROSPRAY-QUADRUPOLE-TIME OF FLIGHT MASS SPECTROMETER

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Analyzing the TAGs in oils is challenging due to the extreme complexity of the materials, the wide range of polarities and molecular weight of the analytes, and most of all due to the presence of numerous isomeric compounds. A new method for the analysis of triglycerides (TAGs) in vegetable oil was developed using a Poroshell 120 EC-C18 column (3.0 x 50 mm, 2.7 micron) with a high resolution ESI-Q-ToF mass spectrometer operating in tandem mass spectrometry as detection system. We used an Agilent Poroshell column, which is characterized by a recently developed stationary phase based on non-porous core particles. The results highlighted the advantages of this column in terms of operating chromatographic conditions and the developed method enabled us to analyze complex mixtures of more than 40 TAGs within less than 25 min and low backpressure (< 100 bar).
The method was optimized on standards of TAGs, validated and applied to several plant oils. By a quantitative point of view, the method showed a very good linearity ($r^2 > 0.999$) in the range 0.1-2.4 µg/g; high intra- and inter-day precision both in terms of retention times (RSD% < 0.04%) and peak areas (RSD% < 0.3%). Limits of detection and quantitation were lower than 0.03 µg/g and 0.10 µg/g, respectively.
Moreover, we applied our method to several reference oils, and the TAG profiles obtained are consistent with those reported in the literature, the main differences being related to different extraction procedures. The optimized method proved to be sensitive, highly selective and robust and is thus suitable for the characterization of oils in the fields of botanical characterization, food analysis, cultural heritage and industrial applications. Moreover the advantages of mass spectrometry also allows the characterization of unknown mixtures of triglycerides.

P36 - QUALITY BY DESIGN AND CAPILLARY ELECTROPHORESIS FOR DEVELOPING ORALLY DISINTEGRATING TABLETS CONTAINING FROVATRIPTAN

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Orally Disintegrating Tablets (ODT) are a drug dosage form that is gaining increasing attention due to the advantages compared to conventional oral dosage forms, mainly represented by the possibility of disintegrating in the saliva in a very short period of time. Frovatriptan (FRO) is one of the safest triptans, administered as a rescue treatment for immediate pain relief of acute migraine headache attacks. Based on these premises, in this study an ODT formulation of FRO was developed with the aim of achieving an easier oral administration together with a faster dissolution and absorption of the drug and, consequently, a more rapid onset of action. The development of ODTs was carried out following innovative Quality by Design principles [1] for the pharmaceutical industry, aimed at making the regulatory approval process more flexible without compromising patient safety. In this context, Design of Experiments strategies play a key role.
The direct compression method was chosen for ODTs production, due to its advantages with respect to other available manufacturing processes, including greater stability of the active ingredient and lower operative costs. After selecting by compatibility studies the suitable excipients, investigation on Knowledge Space (KS) was carried out by means of a screening matrix in order to evaluate the effect of five different variables (diluent, lubricant, superdisgregant kind, compression force and superdisgregant amount) on the selected control quality attributes (tablets disintegration time, tablets hardness and friability, percentage of drug released at 1 min in simulated saliva). The amount of drug released was evaluated by means of a fast capillary electrophoresis method, optimized by applying a Box-Behnken Design with voltage, temperature, pH and concentration of the background electrolyte as selected factors. The screening step on KS constituted the basis for finding Design Space by means of Response Surface Methodology with the aid of Monte-Carlo simulations.

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P37 - EXPERIMENTAL DESIGN METHODOLOGIES IN THE DEVELOPMENT OF MUCOADHESIVE WAFERS LOADED WITH ECONAZOLE

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The aim of this work was to develop mucoadhesive wafers loaded with econazole for the treatment of oral candidiasis. Lyophilized wafers are an innovative drug delivery system able to form hydrogels on contact with saliva and to ensure a controlled drug release. Econazole is an imidazole antifungal agent very poorly water soluble. For this reason, in order to improve its dissolution properties, it was added to the wafers as coground product with sulfobutylether-β-cyclodextrin and citric acid.
The traditional approach for developing a new formulation is to change one variable at a time (OVAT), but this method suffers from several pitfalls, being strenuous, uneconomical, and unable to reveal interactions between the factors. In this study experimental design methodologies (DoE) were applied in order to overcome most shortcomings inherent to the traditional OVAT approach.
A screening design was used at the beginning of the experimental procedure to reveal whether the formulation factors evaluated (pectin kind and carboxymethyl cellulose (CMC) and pectin amount) had an influence on the responses (residence time and adhesive strength to excised porcine mucosa) and to identify their appropriate ranges. From this study it was found that the kind of pectin does not significantly affect the mucoadhesive properties of the wafers; for this reason this variable was not considered in the next experimental stage (optimization phase). After the initial screening, response surface methodology was used to predict the response values for all possible combinations of factors within the experimental region, and to identify the optimal composition. A Central Composite Design was applied, since it makes it possible to obtain response surface plots, which can be easily investigated to individuate the optimal point.
The best composition of the wafer, obtained by application of Derringer's desirability function, was the following: amidated pectin 7.2%(w/w) and CMC 5.2%(w/w). The experimental values of adhesive strength (28.4± 0.04 g/cm^2) and residence time (88.1±0.1 min) given by the optimized formulation were very close to the predicted values, thus demonstrating the validity of the applied model.

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P38 - DATA FUSION PROTOCOLS FOR FOOD AUTHENTICATION

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In recent years, the problems related to the authentication and traceability of food have become of primary interest, both for consumers and producers. In this context, there has been an increasing number of papers in the literature attesting that the most effective analytical approach consists in using fingerprinting analytical techniques coupled with chemometric instrumental techniques that provide a "fingerprint" of foods. This type of approach, indeed, has the undeniable advantage of allowing to obtain accurate results in terms of recognition of the origin of the analyzed products and verification of their label compliance using, in many cases, rapid, relatively inexpensive and potentially non-invasive/non-destructive methods. However, although the results obtained so far for the quality control of many foods can be considered satisfactory, sometimes the acquisition of a fingerprint through a single instrumental technique may not be sufficient to develop a method that possesses the required accuracy. In such cases, it may be useful to use the possibility to acquire signals from more than one instrumental technique on each sample and, therefore, to use the combined information from the two (or more) techniques to build the final chemometric model for the authentication of the food: such an approach is generally called "data-fusion." In this way, especially if the instruments chosen possess complementary features, it is possible to benefit from the advantages and the specific characteristics of each, to create a final model that is more reliable and robust.
In this communication, the results of a systematic study of the possible protocols for data-fusion applicable to the fingerprints resulting from different instrumental analytical techniques, to develop integrated methods capable of evaluating a posteriori the traceability and, in general, the quality of food samples will be presented.
In particular, to evaluate the applicability of the different chemometric protocols attention will be focused on the authentication of two alimentary products with high added value: olive oil and beer.

P39 - AN INTEGRATED QUALITY BY DESIGN APPROACH TOWARDS THE DESIGN SPACE DEFINITION OF A CAPILLARY ELECTROPHORESIS METHOD FOR THE ANALYSIS OF TRIPTANS

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Analytical methods used for the determination of active pharmaceutical ingredients and drug products are an integral part of the Quality by Design (QbD) concept that is outlined in ICH Guideline Q8 for pharmaceutical development [1]. The method used for analysis should meet its intended purpose similar to the product requirements for a clinical dosage form [2]. The application of QbD leads to the definition of Design Space (DS), a multidimensional space which includes any combination of the variables that have been demonstrated to provide assurance of quality of the data produced by the method [2].
In this study a capillary electrophoresis (CE) method has been developed for the separation of the seven triptans available on the market, *e.g.* almotriptan, eletriptan, frovatriptan, naratriptan, rizatriptan, sumatriptan, zolmitriptan. The development was carried out by implementing each step of QbD workflow [2], enabling enhanced quality to be integrated into the analytical method. Control quality attributes (CQAs) were represented by resolution values of critical peak pairs and analysis time. Method scouting indicated microemulsion electrokinetic chromatography (MEEKC) as a suitable CE operative mode. In MEEKC the microemulsion droplets are regarded as the pseudostationary phase and are prepared by mixing oil, aqueous buffer and surfactant/cosurfactant in specific ratios. Mixture design is suitable for blending problems and was applied for finding the ranges for the components of the microemulsion which fulfilled the requirements for the CQAs. Risk of failure maps, obtained by means of Monte-Carlo simulations, were used for defining DS. A control strategy was established by means of system suitability tests.

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P40 - NEAR INFRARED SPECTROSCOPY FOR NON-DESTRUCTIVE CHARACTERIZATION OF TOMATO CULTIVAR. A PILOT STUDY ON 'CUORE DI BUE DI ALBENGA'.

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The feasibility of using a non-destructive method based on near infrared spectroscopy (NIRS) for the identification of the cultivar of morphologically very similar tomatoes was investigated. The study was particularly focused on 'Cuore di bue di Albenga', a heirloom beefsteak tomato. The landrace under study is widely cultivated in the western part of Liguria region, around the city of Albenga. This landrace is particularly appreciated for its outstanding organoleptic qualities.
The identification of tomato varieties has been traditionally carried out by morphological and agronomic traits and identification of genetic diversity and distinctiveness [1]. Spectroscopy can be an interesting alternative for high-speed, non-destructive and multiple measurement of quality parameters[2].
In this study, NIRS measurements were performed on tomatoes obtained from various sources in Liguria. Care was taken in selecting fruits on the basis of a maturity uniformity. Sampling was planned by the Special Company for Professional Training and Technological and Commercial Promotion of the Chamber of Commerce of Savona, who assured the traceability and representativity of samples. Spectroscopic measurements were made with a FT near-infrared spectrometer (Buchi NIRFlex N-500), in the reflectance mode. The multivariate repeatability was evaluated by principal component analysis (PCA), testing several mathematical transformations. PCA showed that the main source of variability is represented by difference in cultivars, while only a lower level of total variance is associated with differences among tomato plants or producers. This non-destructive method based on NIR spectroscopy seems to be a promising procedure for the identification of tomato 'Cuore di bue di Albenga'.

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P41 - EVALUATION OF THE EFFECT OF RED CHILLI ADDITION TO FOOD PRODUCTS ON THEIR SHELF-LIFE

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Food products containing fats can deteriorate during shelf-life because of oxidation reactions involving oxygen consumption.
The instrument Oxitest, based on a measure of accelerating oxidation process using high temperatures and pre-determined oxygen pressure, offers a reliable evaluation of the oxidative damage of a food product.
The determination of the antioxidant capacity of spices such as red chilli in foods could be of great importance by researchers and those involved in the agrofood industry.
In particular, in this work, the effect of the addition of red chilli to extra-virgin olive oil has been tested. The powders of red chilli belonging to three different cultivars, and characterized by different levels of piquancy, has been added to extra-virgin olive oil samples. The determination of the oxidative stability has been carried out by Oxitest during shelf-life at room temperature. The chili pepper powders have also been submitted to FRAP test in order to monitor the antioxidant effect of the red chilli employed.
The results obtained showed that the addition of chili pepper prolonged the stability of all samples compared to that of extra-virgin olive oil alone. The FRAP value showed a good correlation with data registered, and was found not being dependent on the pepper piquancy.
Besides, investigation was extended to verify the oxidation process in 'nduja sausage, which is a typical Calabria’s sausage rich in fat and red chilly , usually made without any additives and preservatives. also in this case The determination of the oxidative stability has been carried out by Oxitest during shelf-life at room temperature and results were compared with those obtained with 'nduja sausage enriched with carbohydrate-based fiber as a fat replacer. The obtained results will be presented and discussed

P42 - CARBOHYDRATE-BASED BRINE COMPOSITION IN HIGH QUALITY COOKED HAM PRODUCTION

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In recent years, consumers have demanded meat products that are safe, nutritious, convenient, rich in variety, attractive (in appearance, texture, odour and taste) and innovative. Cooked ham is one of the most popular processed meat products. The final quality of this meat product is influenced by many factors depending on the raw material used and on processing, which includes injection of brine, tumbling and cooking. Injection of brine ensures a uniform distribution of sodium chloride, nitrites and other possible ingredients (i.e. sugars, spices, polyphosphates, etc.). The brine injection level and the ingredients used are characteristic of each product and determine the cooked ham quality. In particular, products of higher quality are generally made without polyphosphates and with a low level of brine injection.
The poster details the work that was carried out using honey as sugar replacer in brine formulations. Experiments were carried out using honey, from different botanical origin. However, the study was focused on light honeys, so that they do not overwhelm and mask cooked ham flavor. In this work result regarding the use of two type of honeys from different botanical origin , such as acacia honey and chestnut honey will be presented.
The study was extended to characterize inulin of different DP degree as potential ingredient to be added to brine composition and its proper incorporation through cooked ham improving by this way the health image of this meat product. Honey's sugars and carbohydrate distribution of inulin having different DP degree was performed by High Performance Liquid Cromatography coupled with pulsed amperometric detection. (HPAEC-PAD).
Moreover, Environmental scanning electron microscopy (ESEM) was used to study the microstructure of cooked ham produced using different brine composition and comparing cooked ham purchased from different sources.
Results are presented and discussed.

P43 - CHARACTERIZATION OF UNIFLORAL AND MULTI-FLORAL HONEYS FROM MARCHE, CENTRAL ITALY, WITH A CHEMOMETRIC APPROACH ON THE BASIS OF PHYSICOCHEMICAL ANALYSIS.

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The purpose of this study was the physicochemical characterization and classification of Italian honey from Marche Region with a chemometric approach. A total of 135 honeys from different botanical origins [acacia (*Robinia pseudoacacia*), chestnut (*Castanea sativa*), coriander (*Coriandrum sativum*), lime (*Tilia* spp.), sunflower (*Helianthus annuus*), *Metcalfa* honeydew and multifloral honey] were considered. A palinological study of the honey samples was performed in order to guarantee the labelled botanical origin [1]. The physicochemical determinations were carried out on the honey samples on the basis of the Harmonised Methods of the International Honey Commission [2] and of the official methods of analysis published in the Italian legislation [3]. The average results of electrical conductivity (0.14 – 1.45 mS cm^{-1}), pH (3.89 – 5.42), free acidity (10.9 – 39.0 meq_{NaOH} kg^{-1}), lactones (2.4 – 4.5 meq_{NaOH} kg^{-1}), total acidity (14.5 – 40.9 meq_{NaOH} kg^{-1}), proline (229 – 665 mg kg^{-1}) and 5-(Hydroxy-methyl)-2-furaldehyde (0.6 – 3.9 mg kg^{-1}) content show wide variability among analysed honey types, with statistically significant differences among different honey types. Pattern recognition methods such as principal component analysis and discriminant analysis were performed in order to find a relationship between variables and types of honey and to classify honeys on the basis of their physicochemical properties. The variables electrical conductivity, acidity (free, lactones), pH and proline content exhibited higher discriminant power and provided enough information for the classification and distinction of unifloral honey types, but not for the classification of multifloral honey (100% and 85% of samples correctly classified, respectively).

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P44 - DETERMINATION AND DISTRIBUTION OF YLOID IN SOIL AND OVERALL GRAPEVINE SYSTEM (*VITIS VINIFERA* L.) BY ICP-MS TECHNIQUE. A CASE STUDY

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Nowadays, several studies are focusing on YLOID (Y and Lanthanoids) in order to evaluate their potential use as tracers to effectively define the geographical wine origin. Our project has been based on vineyard traceability and began studying the soil-plant system in greenhouse in order to verify whether different cultivars on different soils had similar lanthanides uptake behavior and if they well reproduced the soil YLOID distribution[1]. In a second step, the studies focused on the behavior of YLOID in grapes of two different cultivars on six different rootstocks on the same soil type [2,3]. In this work we investigated into distribution of YLOID in grapevine plant. In particular, the chemical behavior of Y, La and Lanthanoids has been studied to evaluate and trace the distribution from soil to roots, stems and shoots on fifteen years old plants; at the same time the chemical behaviour has been evaluated on two different pruning system, such as cordon and Guyot systems. Samples have been collected from four vineyards located in "Regaleali Estate" (latitude 37°41′50.06″ N; longitude 13°50′51.05″ E and 428 meters above the sea level), Sicily (Italy). The cultivars investigated (Cabernet Sauvignon, Chardonnay and Grecanico) were all grafted on the same rootstock type (1103P). The whole samples have been crushed, homogenized, dried in oven at 105°C and once more homogenized. Aliquots of 0.5 g of each sample (dried weight, DW) were digested using HNO_3 and H_2O_2 in a microwave oven and analyzed with an ICP-MS instrument. The YLOID amounts and distributions in the grapevine-soil system have been determined. The relationship Yb *versus* La and the pattern of distribution of YLOID have been calculated and critically discussed on the basis of the different amount observed in each part of the plants.
The analytical results gave us a good representation of YLOID distribution in a soil-plant system at *equilibrium* which can be useful to improve the knowledge of YLOID as a tracer on *Vitis vinifera* system in field.

[1] P. Censi, F. Saiano, A. Pisciotta, N. Tuzzolino, submitted to Environmental Science and Technology
[2] A. Pisciotta, L. Tutone, F. Saiano, 18th International Symposium GiESCO 2013, Porto, 7-11 July 2013, Portugal
[3] A. Pisciotta, D. Mistretta, N. Tuzzolino, F. Saiano, 3rd International Symposium Ampelos 2013, Santorini, 30-31 May 2013, Greece.

P45 - ENHANCING CONSUMER QUALITY PERCEPTION TOWARDS PROTECTED DESIGNATION OF ORIGIN PRODUCTS BY GEOGRAPHICAL TRACEABILITY: THE CASE OF BOLOGNA POTATOES PDO

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The development of analytical methodologies able to confirm/determinate the geographic origin of food is becoming an increasingly dynamic area in authenticity as well as traceability context. The globalization of agri-food system led to the spread of different varieties of food and raw materials around the world but sometimes also to a loss in their quality. Therefore, geographical origin of food often became synonymous of quality and safety and its authentication remains an important goal for producers and consumers too. Aim of this study is to develop a geographical traceability model for a typical food of Bologna district, namely the *Bologna PDO potatoes*. The product obtained the designation of origin in 2009 and according to the respective European Regulation [1], its production can be obtained from a variety, 'Primura', grown in soils of Bologna district. In particular, in this study, among the different geographical indicators, strontium isotopic ratio, $^{87}Sr/^{86}Sr$, has been used, given to its tracer potentialities able to link a food to its territory of origin [2]. Thanks to the collaboration with the Consortium of the potato producers of Emilia Romagna (ASSOPA), within a project funded by Emilia Romagna region [3], samples of potato tubers of two varieties ('Agata' and 'Primura'), harvested in 2012, and soils (0–20 cm depht) were collected in different cultivated areas of Emilia Romagna. In particular, three different geological substrates soils were considered: "Alluvional Plain of the Appennine Rivers" (Bologna, Ravenna), "Po Plain" and "Coastal Plain" (Ferrara). All sampling sites were chosen on the basis of productivity and availability of the farmer criteria. $^{87}Sr/^{86}Sr$ values in potatoes and soils samples have been determined by using a double focusing magnetic sector multicollector. The isotopic values obtained for potatoes perfectly matched with their respective soils in almost all the cases. Furthermore, the used indicator was able to discriminate samples coming from lowlands and the Emilia Romagna's coast. Nevertheless, more work is needed, such as the careful understanding of the impact of agricultural practices (e.g. conditions of use of fertilizers and of irrigation water) and the validation of model with the analysis of samples coming outside the Bologna district.

[1] Regolamento di esecuzione (UE) N. 766/2012 DELLA COMMISSIONE del 24 luglio 2012.
[2] C. Durante, C. Baschieri, L. Bertacchini, M. Cocchi, S. Sighinolfi, M. Silvestri, A. Marchetti. Food Chem.(2013) doi: http://dx.doi.org/10.1016/j.foodchem.2013.05.108
[3] Progetto di ricerca finanziato mediante la misura 124 del PSR 2007-2013 della Regione Emilia Romagna "*Caratterizzazione geografica della Patata della regione Emilia Romagna*"/ Italia.

P46 - RAPID DETERMINATION OF XANTHINE METABOLITES IN FOOD BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL AND UV DETECTION

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Purine bases and their derivatives play an important role in the functioning of living systems. Purines are involved in many metabolic processes as cofactors which play key roles in fundamental biological processes. In particular, uric acid (UA), xanthine (XA) and hypoxanthine (HX) are degradation products of purine metabolism in human beings and higher primates.
The determination of xanthine can be interesting not only in biological fluids, since involved in various diseases, but also in food industry for quality control of the products. Several analytical methods such as colorimetry, fluorometry, HPLC, mass spectrometry, anion exchange chromatography, thin layer chromatography and capillary column gas chromatography have been employed for measurement of purines [1, 2].
In the present study a simple and sensitive method using high-performance liquid chromatography with electrochemical detection (HPLC-ED) at several electrochemical sensors and with ultraviolet detection (HPLC-UV) has been developed for the determination of purines in fish meat for the evaluation of freshness.
The experimental parameters were systematically optimized for each analyte of UA, XA and HX. For an efficient separation and detection of these analytes, a Hypersil ODS column, a mobile phase consisting of 0.004 M potassium phosphate buffer pH 5.8 with 1% (v/v) of methanol in isocratic mode were used. This system couples the suitable separation power of HPLC to an inherent sensitivity of electrochemical detection in a short run time, and is capable of measuring purine metabolites with minimal sample preparation and low injection volume.
The estimation of the fish freshness by monitoring the purines content was also established with a low concentration level and very good reproducibility.

[1] R. Devi, S. Yadav, C.S. Pundir, Analyst 137 (2012) 754-759.
[2] T.C. Burdett, C.A. Desjardins, R.Logan, N.R. McFarland, X. Chen, M.A. Schwarzschild, Biomedical Chromatography 27 (2013) 122-129.

P47 - DETERMINATION OF MELAMINE IN FOOD BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY – UV DETECTOR

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Melamine (2,4,6-triamino-s-triazine) is an organic compound, that contains 66% nitrogen by mass, commonly used in the production of plastics, dyes, fertilizers, and fabrics. Recently, melamine was illegally added to food to elevate falsely assay results for protein content.
Melamine contamination has been reported in products such as milk, infant formula, frozen yogurt, pet food, biscuits, candy, and coffee drinks [1-3].
A variety of toxic effects from melamine, including nephrolithiasis, chronic kidney inflammation, and bladder carcinoma Therefore, it is necessary to develop some simple, economical and efficient methods for the analysis and quantitative measurement of these compound in order to insure human health and food safety. In this study, a sensitive, and simple method for the determination of melamine by liquid chromatography with UV – detection has been developed.
A cation-exchange chromatography methodology for the fast determination of melamine, in acidic medium was studied and optimized. Under optimal conditions, the limit of detection of the investigated molecule is 0.01 μM and the dynamic linear range spanned generally over three orders of magnitude. Sample pretreatment procedure based on SPE before the LC separation is studied for the quantitative extraction of melamine from milk, infant formula, and dietetic supplements.

[1] Food and Agriculture organization of the United Nation, World Health Organization, Toxicological and Health Aspects of Melamine and cyanuric acid, Health Canada, Ottawa, Canada, 1-4 December (2008).
[2] M. Curcio, F. Puoci, G. Cirillo, F. Iemma, U.G. Spizzeri, N. Picci, J. Agric. Food Chem. 58 (2010) 11883-11887
[3] M. Ibáňez, J.V. Sancho, F. Hernandez, Anal. Chim. Acta 649 (2009) 91-97.

P48 - VALIDATION OF A SCREENING METHOD FOR THE DETERMINATION OF NDL-PCBs IN MUSSEL SAMPLES BY GC/ECD ACCORDING TO THE RECENT REGULATION (EU) N°1259/2011

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The contamination by NDL-PCBs, used as lubricants, polymers and adhesives, their toxic effects and their bioaccumulation in aquatic ecosystems has been the subject of intense research for almost the last 20 years (1-2). Mussels as rather ubiquitous and sedentary organisms have been extensively used as a bioindicator species for monitoring of these compounds (3). In order to minimize the risk associated with seafood consumption, the recent Regulation (EU) N°1259/2011 (4) has been implemented to establish the maximum level of 75 ng/g wet weight for the sum of six indicator PCBs (28-52-101-138-153-180). The aim of this work was to validate the present method according to the recent Regulation (EU) N°1259/2011 (4). The method is based on a simple and rapid extraction with n-hexane, sulphuric acid (90%) and ENVI-carb, before the identification and quantification of the residues by gas-chromatography equipped with an electron capture detector (GC/ECD)(5). A validation protocol was carried out in order to establish the performance characteristics of this method which ensure the correct identification and quantification of NDL-PCBs in mussel samples. Parameters such as linearity, precision, recovery, limit of detection (LOD) and quantification (LOQ), specificity and ruggedness resulted in compliance with SANCO 12495/2011(6) and Decision 2002/657/EC (7). Linearity was studied in the range of 5,0-100,0 ng/ml and calibration curves were linear (R^2 $\geq$0,99) in the whole range of explored concentrations. Instrumental LODs and LOQs ranged from 0,11 to 0,18 ng/ml and from 0,33 to 0,54 ng/ml respectively. Precision was evaluated by injecting six replicates spiked at five levels i.e. 6,0-15,0-30,0-60,0-90,0 ng/g in matrix, in order to include the maximum level for the sum of six indicators in the explored range; good recoveries (78-100 %) were obtained. LODs and LOQs of the method in spiked samples were also calculated and ranged from 0,11 to 0,21 ng/g and from 0,31 to 0,63 ng/g respectively. Method specificity was verified by absence of significant interference in the maximum tolerance range (± 0,5%) for GC retention times of analytes compared with those of spiked samples. Method ruggedness was estimated for minor changes by means of the Youden test. Seven different factors were chosen in the entire analytical process, because of their possible critical influence.

[1] O.S. Okay, et al., Chemosphere 76 (2009) 159-166.
[2] V. I. Valsamaki, et al., Analytica Chimica Acta 573-574 (2006) 195-201.
[3] M.E. Chase, et al., Mar. Pollut. Bull. 42(2001) 491-505.
[4] Commission Regulation (EU) N 1259/2011.
[5] V. Nardelli, et al., Atti Ciseta (2011).
[6] SANCO Document 12495 (2011).
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P49 - AQUEOUS EXTRACTION AT ROOM TEMPERATURE OF STEVIOSIDES CONTENT IN DRIED LEAVES OF STEVIA REBAUDIANA BERTONI USING THE EXTRACTOR NAVIGLIO. COMPARISON WITH CONVENTIONAL HOT INFUSION.

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Stevia is the common name of stevioside extract obtained from the leaves of *Stevia rebaudiana* Bertoni. It is a natural sweetener, calorie-free, which can also be used as a sugar substitute or as an alternative to artificial sweeteners. The use of Stevia as a sweetener has recently been approved by the Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives and, recently, has also been approved as GRAS (Generally Recognized As Safe) by the Food and Drug Administration. Furthermore, the Stevia is inexpensive and is easily available for the majority of consumers, therefore, has the potential to be widely used, also helping in weight regulation, as it has a positive effect on the caloric intake. In this work are compared two methods of extraction by HPLC analysis of aqueous extracts of dried leaves of Stevia obtained with the traditional method at high temperature (hot infusion: 70° C for 20 min.) and the Naviglio extractor (NE) at room temperature [1]. The results obtained showed a higher efficiency of the Naviglio extractor for obtaining a higher amount and with greater purity of stevioside, with an optimum time of extraction between 60 and 90 minutes. Indeed, in these conditions, the recovery of stevioside is equal to more than three times of that obtained by the process of hot extraction.

[1] Naviglio, D. Naviglio's principle and presentation of an innovative solid-liquid extraction technology. Extractor Naviglio. Analytical Letters 36(8) (2003), pp. 1647-1659.

P50 - INVESTIGATION OF DIFFERENT SAMPLE TREATMENT METHODS FOR THE LIQUID CHROMATOGRAPHY-ELECTROSPRAY-TANDEM MASS SPECTROMETRY DETECTION OF ALLERGENIC FINING AGENT RESIDUES IN RED WINE

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Red wine production in Italy plays an important role in the agricultural economy of several regions both at the local and international level. Red wine is a complex matrix rich in polyphenols, tannins, anthocyanins and other compounds that can interact with proteins making challenging their quantitative analysis. Recently, attention has been paid to the putative presence of traces of exogenous proteins (i.e. caseins, albumins, lysozyme, gluten) added during wine fining process and removed before bottling. These proteins present allergen activity [1, 2] and the accurate determination of their residual concentration is desirable to ensure consumer safety.
In this work, different sample treatment protocols for the liquid chromatography-electrospray-tandem mass spectrometry (LC-ESI-MS/MS) analysis of potential residuals allergens in red wine were developed. Attention was paid to the simultaneous detection and quantitation of fining agent residues, i.e. ovalbumin, α- and β-casein, in wine samples. The experimental workflow was based on the selection of targeted peptides and the use of selected reaction monitoring (SRM) acquisition mode for quantitative purposes [3]. The different sample treatment methods were compared in terms of protein recovery. The use of denaturing agents combined with size exclusion concentration and purification allowed to obtain a reproducible (RDS < 20%) analytical protocol with good recoveries (73(±2) - 109(±4) %) for digested proteins from 12.5 ml of wine sample. Matrix-matched calibration from LC-ESI-MS/MS analysis indicated that the devised method allowed detection of target peptides in the 0.01-0.8 μg/ml range. Finally, method selectivity was demonstrated by analyzing 20 commercial red wine samples from different wine-producing Italian regions and produced during 2007-2011 vintages.

[1] Directive 2003/89/EC, Off. J. Eur. Union L308 (2003) 15-18.
[2] Directive 2007/68/EC, Off. J. Eur. Union L310 (2007) 11-14.
[3] M. Mattarozzi, C. Bignardi, L. Elviri, M. Careri, J. Agric. Food Chem. 60 (2012) 5841-5846.

P51 - USE OF ROOM TEMPERATURE IONIC LIQUIDS (RTILs) FOR ELECTROCHEMICAL MEASUREMENT OF FREE ACIDITY IN OLIVE OIL

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Room temperature ionic liquids (RTILs) have received growing attention in the recent years, due to their ability to be tailored for an ever-expanding range of applications. One important research area is in the electrochemistry field, as they may exhibit a number of advantages over non-aqueous solvents that are traditionally employed for electrochemical investigations. RTILs are, in fact, typically characterised by low volatility and toxicity, high chemical and thermal stability, wide electrochemical windows, high intrinsic conductivity and the ability to dissolve a wide number of organic and inorganic compounds.
These electrochemically relevant properties allow RTILs to be used as electrolytes also in essentially low-conductive natural matrices, which are normally inaccessible to direct voltammetric measurements - such as vegetable olive oils. In fact, such matrices are characterised by high viscosity, low conductivity, low solubility in the standard solvents as well as by the inability to solubilise sufficient amounts of electrolytes employed usually in electrochemistry.
In the present study, the use of RTILs is proposed to perform direct electrochemical measurements in olive oils, aimed at quantifying the acidity level in such natural samples. In more detail, the RTIL trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide ($[TETDP]^+[imide]^-$) was mixed 1:1 (*w*/*w*) with olive oil. Microdisk electrodes (Pt, r = 11 μm) were employed in order to minimise ohmic drop problems due to the high viscosity of the oil/RTIL mixture; furthermore, they allow to perform analyses on small oil volumes (< 1 mL).
Under such conditions, cronoamperometry (CA) measurements showed a correspondence between the measured current (evaluated at -1.5 V vs. Ag pseudoreference) and the free oleic acid content in oil samples.
Such a method seems to be a promising alternative to the official method for determination of olive oil acidity – acidimetric tritration, in non-aqueous solvents, with a standard KOH solution in ethanol [1,2].

[1] EEC Regulation n. 2568/91.
[2] EEC Regulation n. 183/93.

P52 - STUDY OF PROTONATION EQUILIBRIA OF SCHIFF BASE DERIVED FROM O–VANILLIN AND 1,2–DIAMINOBENZENE.

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Schiff bases have been extensively studied for their biological and pharmacological activities [1], as well as suitability for analytical applications. The Schiff bases derived from o-vanillin and 1,2-diaminobenzene (6-(((2-aminophenyl)imino)methyl)-2-methoxyphenol =L) presents various protonation equilibria. Their application require a detailed study of their solution chemistry. The spectroscopic and spectrofluorimetric behavior in a wide pH range in the NaCl solutions are presented. The compound exhibits a low solubility in aqueous solution and is unstable after about a week. To study the acid base properties of this system have been performed spectrophotometric and potentiometric measurements in solutions containing low concentrations of buffer systems that do not affect the acid–base behavior of the ligand. The measurements were carried out at 25° C in NaCl as ionic medium (0.1 –1 M). The changes in the spectrum of solutions of the ligand in dependence of the pH were used to determine the constants of protolysis of the compound.

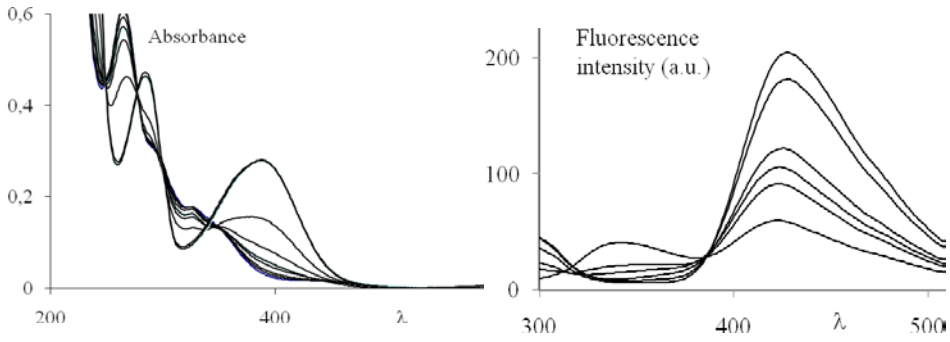

Figure. Variation of absorbance (left) and fluorescence intensity (right) of L in function of pH in NaCl 0.1M.

The results obtained were confirmed by measures spectrofluorimetric, which show emission bands related to different deprotonated forms of L. The overall experimental data were processed with the Hyperquad program.

[1] D. Sinha, A.K. Tiwari, S. Singh, G. Shukla, P. Mishra, H. Chandra, A.K. Mishra, Eur.J. Med. Chem. 43 (2008) 160.

P53 - INTERACTION BETWEEN IRON(III) CATION AND SCHIFF BASE DERIVED BY O–VANILLIN AND 1,2–DIAMINOBENZENE.

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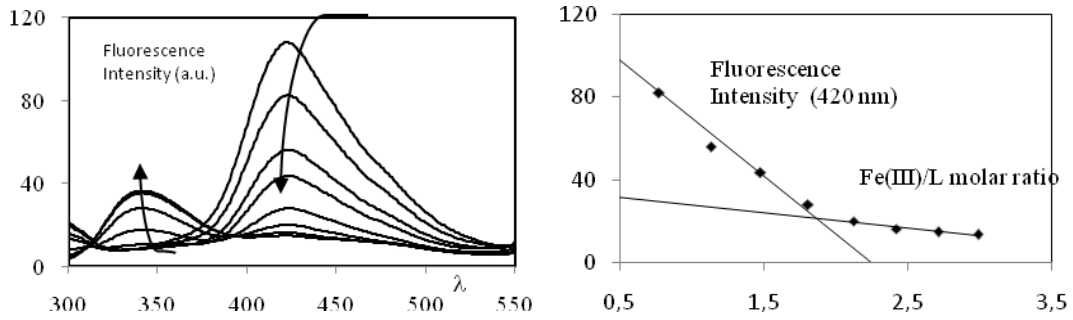
Schiff bases and their metal complexes are very important as catalysts in various biological, medicinal and pharmaceutical fields [1]. This work presents the interaction of Fe(III) cation with the Schiff bases derived from o-vanillin and 1,2-diaminobenzene (6-(((2-aminophenyl)imino)methyl)-2-methoxyphenol =L). This ligand is poorly soluble (10^{-5} M) in aqueous solution and complexation studies are difficult for the low concentration of species that are formed. Favorable conditions for equilibrium analysis are obtained by increasing the concentration of the metal compared to that of the ligand. The experimental data were carried out in the form of spectrophotometric and potentiometric titration by varying the hydrogenionic concentration in the range $1 \leq pH \leq 6$. The measurements were carried out at 25° C in 0.1 M NaCl as ionic medium. The variation of the spectrofluorimetric spectra as a function of concentration of the metal is shown in Figure. The change in fluorescence intensity a function of the metal / ligand molar ratio, at constant pH, shows the formation of a complex with 2:1 stoichiometry ratio.
Similar results are obtained from UV-VIS spectrophotometric measurements; a speciation model is obtained by processing the experimental data using Hyperquad program.



The increase of fluorescence intensity at 340 nm can be used for the determination of Fe (III) in aqueous systems.

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P54 - THE BEHAVIOR OF ARGININE AS LIGAND TOWARD IRON (II) AND IRON (III)

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L-Arginine, 2(S)-amine-5-guanidilpentanoic acid, in the deprotonated form ($L = C_6H_{13}N_4O_2^-$) has one carboxylic, one amino and one guanidine group. Few investigations are reported in the literature on the properties of arginine as ligand. The three protonation constants of arginine have been accurately determinated at 25°C either in 1.00 mol dm^{-3} NaCl and in 1.00 mol dm^{-3} $NaClO_4$, as ionic media, by means of electromotive force measurements (e.m.f) employing a glass electrode. In addition, a hydrogen electrode was used in alkaline solution. In the same paper, silver and glass electrodes were used to study the behavior of L-arginine as ligand toward silver(I) [1].
The knowledge of the protolytic equilibria of arginine and its complex formation with silver(I), was very useful to investigate the behavior of arginine toward calcium(II) and magnesium(II) [2].
Few research about the behavior of arginine as a ligand of iron(II) and iron(III) were carried out. The investigation on the system iron(II) and arginine was performed at 25°C and in 1.00 mol dm^{-3} $NaClO_4$, as ionic medium, by means e.m.f. with a glass electrode. The formation of complexes between the iron(III) and arginine was investigated at 25°C and in 1.00 mol dm^{-3} $NaClO_4$, as ionic medium, by measuring the e.m.f. of the following cells:
R.E./Solution S/G.E.; R.E./ Solution S, Fe(III)-Fe(II)/Pt.
Experimental data related to iron(II), were explained by assuming the formation of FeHL ($\log\beta_1 = 3.40 \pm 0.05$). Experimental data related to iron(III), were explained by assuming the formation of $Fe(H_2L)_2$, $Fe_2(H_2L)_2$,
$FeH_{-1}(H_2L)_2$, and $Fe_2H_{-2}(H_2L)_2$. Polynuclear and complexes either with assumption and with loss of protons are formed. The ligand acts in protonated forms HL and H_2L either for Fe(II)-arginine and Fe(III)-arginine.
The species assumed to explain the experimental data obtained studying the system iron(III)-arginine and relative stability constants are here reported: $Fe(H_2L)_2$ ($\log\beta_{1,0,2} = 2.20 \pm 0.10$), $Fe_2(H_2L)_2$ ($\log\beta_{2,0,2} = 6.25 \pm 0.10$),
$FeH_{-1}(H_2L)_2$ ($\log\beta_{1,-1,2} = -0.60 \pm 0.08$), and $Fe_2H_{-2}(H_2L)_2$ ($\log\beta_{2,-2,2} = 0.55 \pm 0.10$). Binuclear species with the loss of protons are prevalent. A hypothesis on the formation of $Fe_2H_{-2}(H_2L)_2$ is proposed.

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[2] M. Antonilli, E. Bottari, M.R. Festa, L. Gentile, Chem. Spec. Bioavail., 21(1) (2009) 33-40.

P55 - A CATIONIC PORPHYRIN IN A MICELLAR MEDIUM: PRELIMINARY ANALYSIS OF SYSTEM CHARACTERISTICS AND METAL EXTRACTION ABILITY

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Porphyrins hold important tasks in nature, industry, chemistry, and medicine. They can selectively coordinate metal ions and, due to their optical properties, they can act as stains and sensors [1]. Recently, cationic porphyrins found use in biochemistry [2] and as therapeutic drugs [3]. Moreover, gold porphyrins showed interesting anti-cancer properties [4].
Micelles, formed by surfactants upon a certain critical concentration, can be used for biological studies on small molecules, as they represent a first approximated model of the cellular membrane. Moreover, they can find application for extraction purposes, based on the concentration of a toxic and/or precious metal in the micellar pseudo-phase and its recovery upon ultra-filtration techniques.
Porphyrins have been intensely studies in aqueous medium but much less attention has been devoted to their characteristics in micellar systems.

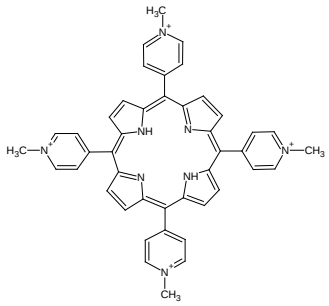

Figure 1 Molecular structure of the analysed porphyrin

We have analysed the characteristics of 5,10, 15,20-tetrakis(1-methyl-4-pyridyl)-porphyne (H_2TMPyP^{4+}) (Figure 1) in micellar anionic (sodium dodecyl sulphate) and cationic (tetradodecylammonium chloride) media. In this preliminary study, the acid and gold(III) complexation properties of the ligand have been analysed in SDS, together with its ability to complex palladium(II). The degree of repartition of H_2TMPyP^{4+} on the SDS and DTAC micelles with respect to the free ligand has been determined. Atomic absorption measurements suggest that, using this micellar porphyrin system, some palladium recovery and separation with respect to gold can be achieved.

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P56 - SPECTRAL MODIFICATIONS OF SUBTERRANEAN WATERS UNDER IRRADIATION

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Water samples from subterranean systems were optically characterized and irradiated under simulated sunlight. Irradiation of CDOM by sunlight causes both a decrease of the absorbance (photobleaching) [1] and mineralization [2,3]. Interestingly, it has been found that groundwater CDOM is much more susceptible to photomineralization than CDOM in lake water [3]. The effect that sunlight exposure may have on the properties and photochemical behavior of chromophoric dissolved organic matter (CDOM) was studied.
Eight samples of subterranean water were analyzed: six are from caves and two from an aquifer. For each cave, two samples with different characteristics were collected. On each sample, measurement was carried out of DOC (Dissolved Organic Carbon), IC (Inorganic Carbon), nitrate, nitrite, UV-vis spectra, and fluorescence EEM (Emission Excitation Matrices). The latter measure allows the characterization of dissolved organic matter. Samples were then irradiated under simulated sunlight, using a lamp that delivers in 7.3 hours of continuous irradiation the same amount of UV energy per unit surface area, as given by the sun in a fair-weather summer day (e.g. 15 July) at 45°N latitude. The time trends of absorption spectra and spectral slope *S* were determined under irradiation and in the dark. For most samples, the spectral shape of subterranean water was very different from the typical exponential decay with wavelength that was observed in lake water. However, irradiation modified the spectral shape of subterranean water to finally produce a lake water-like exponential trend. The production of an exponential absorption spectrum in those samples was accompanied by an increase of CDOM molecular weight and/or aromaticity, as suggested by a decrease of the *S* values.
It is, therefore, suggested that pre-exposure to sunlight before sampling could play a very significant role in shaping the typically observed exponential spectra of surface waters.

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P57 - ANALYTICAL TESTS FOR THE CHARACTERIZATION AND VALIDATION OF MERCURY-SORBENT MATRICES[1]

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We optimized atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) apparata for the characterization of the metal mercury adsorption properties of carbon-based sorbents in the gas phase and in solution. These apparata were developed in the framework of an European project devoted to the optimization and production of a novel sorbent deriving from the pyrolitic conversion of waste tyres into activated carbon for the removal of mercury from gas streams impregnated with a sodium sulfide solution in order to improve its mercury binding capacity.
In order to test the sorption properties in the gas phase, a selected amount of mercury released in an argon flow by a permeation tube kept at selected temperatures was delivered directly to the AAS or through a cartridge preloaded with activated carbon commercial samples or with the material to be tested. AAS was used as mercury analyzer to continuously measure the elemental mercury Hg^0 at the outlet. This instrumental set up allowed us the study of adsorption kinetic and the capacity of the sorbents.
The mercury adsorption/binding capacity was also evaluated in solution in the perspective of an employment of the sorbent also for mercury removal from waste waters. For these experiments flow injection analysis coupled to Atomic Fluorescence Detector (FIA-AFS) was carried out on samples (0.6-1 mg/mL) suspended and vortexed in MilliQ water/4% methanol with 0.5 mM Hg(II) for 3 days. After centrifugation the surnatant was diluted 10 times and analyzed by FIA-AFS.
The characterization of mercury sorbents was completed with the analysis by a DMA-80 mercury analyzer (FKV) of solids after the adsorption of mercury.

[1] EU project LIFE+2011 ENV/IT/109 "Low cost sorbent for reducing mercury emissions"

P58 - X-RAY PHOTOELECTRON SPECTROSCOPY CHARACTERIZATION OF AEROSOL PARTICLES IN ANTARCTICA

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The trace element content of aerosols sampled in the most remote parts of our planet, primarily due to long range transport, would give valuable information on the global transport of particulates and on the contribution of human activities to air pollution. In these areas moreover extremely interesting records of the past history of the atmosphere of our planet are preserved in snow and ice. In this context, several authors have investigated the occurrence of trace metals in pristine Antarctic snow and ice [1,2] to show the ancient and recent changes in heavy metal quantities in naturally occurring and man-derived aerosols that reach the Antarctica continent. Surface composition of particulate matters is of particular interest, as better represents history of interaction with environment of PM during its transports. X-ray photoelectron spectroscopy (XPS) is a powerful technique for determining the surface chemical composition of atmospheric particles. XPS has emerged since its invention [3]as a tool to analyse PM collected onto filters. Its application continues even recently (see e.g. refs. 4, 5). Surprisingly no application to Antarctic PM has been reported up to now. The present communication reports XPS data on PM collected in Antarctic site of Faraglioni (74°42.968’ S, 164°06.895’ E) in the period 2010/2011with the framework of PNRA 2009 (Project PROGDEF 09_153).

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P59 - ULTRA PERFORMANCE LIQUID CHROMATOGRAPHY WITH FLUORESCENCE DETECTION FOR SIMULTANEOUS DETERMINATION OF ASYMMETRIC DIMETHYLARGININE, MONOMETHYLARGININE, SYMMETRIC DIMETHYLARGININE AND L-ARGININE IN BIOLOGICAL FLUIDS

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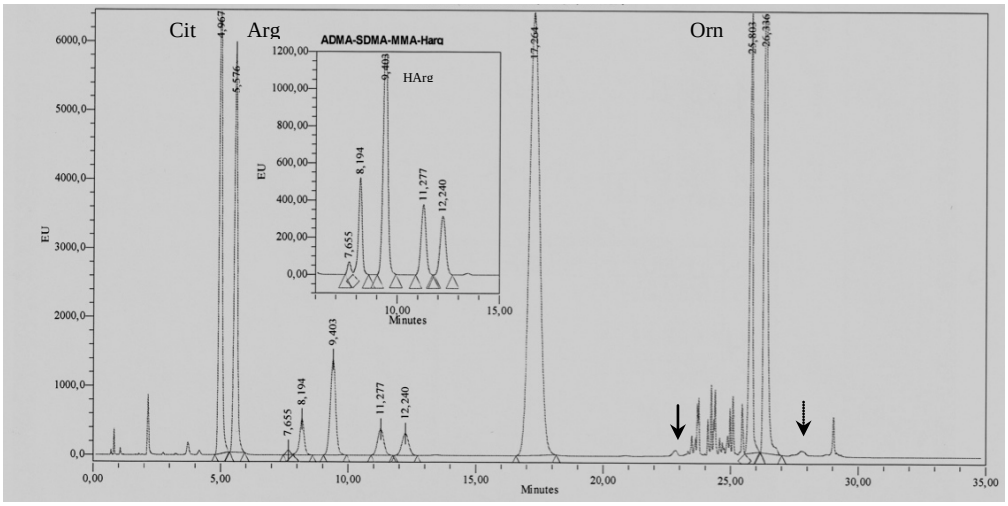
Measurement of N^G,N^G-dimethy-L-arginine (asymmetric DMA, ADMA) in human plasma is of considerable interest, as its increased concentration is believed to be a cause of endothelial dysfunction in a number of pathological conditions, such as hypertension, hyperlipidaemia, renal failure, diabetes mellitus, hyperhomocystinaemia, erectile dysfunction and ischaemic heart disease [1,2]. Asymmetric dimethylarginine is an endogenous and potent competitive inhibitor of the enzyme nitric oxide synthase (NOS), which synthesises nitric oxide (NO) from arginine in the vascular endothelium [3]. Measurement of asymmetric dimethylarginine is hampered by its low concentration in biological fluids and difficulty in chromatographic separation of the two isomers asymmetric dimethylarginine and N^G,$N^{G'}$-dimethy-L-arginine (symmetric DMA, SDMA). In the present study, we described a simple and reliable procedure for extraction of arginine, and its methylated derivatives (ADMA, SDMA, and N^G-monomethy-L-arginine (L-NMMA)), from biological fluids and simultaneous separation of these analytes by gradient mobile phase UPLC system. Sample clean-up is by solid-phase extraction (SPE) on cation exchange cartridges, yielding high recoveries. Fluorescent derivatization is with o-phtalaldehyde (OPA) and 3-mercaptopropionic acid. We use the internal standard monoethylarginine (MEA).



Citrulline (Cit), Arginine (Arg) 25 µM ; NMMA, ADMA,SDMA 1 µM ; HArginine 2 µM ; MEA (IS) 25 µM; Ornithine (Orn), Lysine (Lys) 20 µM gradient: (—) start ; (---) end

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P60 - ANALYSIS OF THE ZnLMM AUGER SIGNAL OF ZnO NANOMATERIALS SYNTHESIZED BY DIFFERENT METHODS

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ZnO-based nanomaterials are receiving significant attention thanks to the peculiar properties exerted by this oxide, especially at nanometer size. Nanostructured ZnO is being continuously proposed for different applications, such as in optoelectronics [1], sensors [2], in Laser Desorption Ionization Mass Spectrometry [3], thanks to its extreme versatility. Considering the importance of the surface chemistry of this nanomaterial, in this communication we report the spectroscopic study by X-ray Photoelectron Spectroscopy (XPS) of nanostructured ZnO prepared according to different approaches (e.g. electrosynthesis, sol-gel, ion beam sputtering). Particular attention will be devoted to the ZnLMM Auger region, as it is a discriminating parameter both for the chemical speciation and for possible size-effects.
It is well known that $Zn2p_{3/2}$ photoelectronic signal alone is not useful to distinguish among different Zn(II) species [4, 5]. Bulk ZnO and other reference compounds have been evaluated to measure their values for $Zn2p_{3/2}$, ZnLMM and the modified Auger parameter (α'). Curve-fitting procedures have been also applied to both photoelectronic and Auger signals. XPS characterization of ZnO-based nanomaterials has been combined to other spectroscopic (UV-Vis, IR) and morphological analyses (TEM, SEM) to investigate the correlation between the material properties and photoelectronic, as well as Auger transitions.

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P61 - A MULTI-ANALYTICAL APPROACH FOR THE STUDY OF HYDROPHOBIZING COATING FOR CULTURALE HERITAGE

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The deterioration process of stone monuments includes the combined action of physical, chemical and biological factors, which induce severe modifications on the surface and structural integrity of the materials [1]. The most appropriate way to avoid deterioration is to prevent water penetration into the stone bulk, since accumulation of water is mainly responsible for stone decay. Different kinds of materials have been used up to now as protective hydrophobic coatings on architectural surfaces.
In this study we have treated stones commonly employed during centuries (Carrara, Candoglia and Botticino marbles and Angera Stones) with different commercial water-repellent protective agents (siloxanes).
A multi-analytical protocol has been set up in order to test the different coating performances. In this regard the protected surfaces have been characterized by several techniques, such as XRD, SEM-EDS, FTIR, TGA, IC, XPS, AFM, water absorption by capillary, CIE-Lab colorimetric analyses, contact angle measurements and surface energy elaborations. In order to investigate the stability of the coatings both accelerated aging tests by UV irradiation (500W, 250-315 nm) and prolonged exposure in a typical urban polluted environment were carried out. Colorimetric measurements (CIELab) were performed to verify the color modification (yellowing) of the protective film due to solar exposition. Not significant variations (i.e. $\Delta E^* < 5$) were registered.
The effectiveness of the different tested coatings in reducing water absorption and salts formation has been also demonstrated.

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P62 - CHARACTERIZATION OF AERONAUTICAL AND AEROSPACE METAL MATERIALS THROUGH THE COMPARISON BETWEEN THE XRF vs. ICP-OES AND FESEM-EDS TECHNIQUES

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Objective The aim of this study is the quantitative and semi-quantitative chemical analysis of aeronautical massive samples in order to compare the X-Ray Fluorescence Spectrometry (XRF) technique with the Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Scanning Electron Microscopy coupled Energy Dispersive X-ray Spectroscopy (SEM-EDS) techniques.
Materials and methods The quantitative analysis was carried out by relating the measured radiation of unknown samples to analytical curves. Calibration curves were performed using Certified Reference Materials (CRM) in the suitable concentration range for each element.
Results The quantitative analysis performing by the XRF technique allows to determine the exact chemical composition of metal materials, as well as the ICP-OES, the principal technique used for the characterization of alloys [1] e [2]. This study has shown the XRF technique, already normed for steels [3], can be used also for aluminium and titanium alloys. The semi-quantitative analysis by XRF can be used for screening analysis of unknown samples; on the basis of these results, it can perform – with the same instrument and on the same sample – the quantitative analysis, according to the suitable alloy. Moreover, the semi-quantitative analysis by XRF, operating at a higher power, gives an error measure lower than the results of the EDS technique.
Conclusions The XRF technique, being a rapid and non-destructive exam, plays a fundamental role by the methods used to quality control of metal materials because it gives the exact chemical composition of them. The semi-quantitative analysis, performing with the same technique, allows the assessment of material's quality and to determine the order of magnitude of the analytical concentration of elements in the sample. So, the XRF technique can be used in the chemical analysis of metal materials as well as ICP-OES, not only for steels, but also for aluminium and titanium alloys. Furthermore, the XRF technique - not including the mineralization of samples - minimizes the operator's chemical risk, reducing times and costs of analysis, too.

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P63 - SPECTROSCOPIC INVESTIGATION ON CONDUCTING POLY(O-AMINOPHENOL) ELECTROSYNTHESIZED ON PLATINUM- ELECTRODES IN ACIDIC MEDIA

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Aminophenols are interesting members of the class of substituted anilines. Within the various isomers, o-aminophenol (OAP) has attracted most attention because of its ability to form conductive polymers under electrochemical oxidation in acidic media [1]. Unlike anilines, OAP is characterized by the presence of two groups both prone to oxidation which complicates the identification of possible intermediates in the polymerization process. There is in fact a controversy in literature regarding the formation of dimeric structures by electrochemical oxidation of OAP in aqueous solutions, acting as soluble precursors of the finite polymer, POAP.

Presently, it is widely agreed that POAP is a ladder polymer composed of phenoxazine units [2]. Besides a completely ring-closed structure, an open one was also formulated containing N-phenyl-p-phenylenediamine repeating units [3]. The possibility of side reaction and consequently of sideward polymerizations thus hinders the comprehension of the real structure of the film. To deepen the understanding on POAP, extensive studies using electrochemical, spectro-electrochemical, impedance measurements and other means of investigation were performed [4] .

In the present work, to gain a further insight into the polymerization route of POAP, a careful investigation has been carried out by employing XPS, micro-Raman and IR as complementary spectroscopic techniques. POAP films were electro-synthesized on platinum substrate by cyclic voltammetry, CV, in acidic OAP solution ($HClO_4/KClO_4$). Following the CV profile, comparative analyses of POAP, by varying its redox state and protonation degree, were performed, highlighting different sampling areas and depths, according to the specificity of each spectroscopy.
The combined results have provided information on the polymer skeleton and its inner (Pt) and outer (environments) interfaces. Notably, the analytical capability of XPS has allowed to formulate the POAP repeat sequence and to identify species adsorbed or trapped inside the polymer.

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P64 - MICROFLUIDIC DEVICE: DEVELOPMENT AND TESTING OF NANOSTRUCTURED OXIDIC MATERIALS

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Mesoporous nanostructured oxides with controlled porosity has been recently proposed in the field of microfluidic analyses, to obtain interconnects for controlled transport of molecular or ionic species, charged nanoparticles or biomolecules. These materials have been proposed for the development of selective gates, to be employed in microchip-based technologies for molecular separation, detection and dosing.
The first step is the synthesis of silica porous films, obtained by sol-gel reaction of tetraethyl orthosilicate (TEOS) using polystyrene-block-poly(ethylene-oxide) (PS-b-PEO) copolymers as templates. To obtain thin films with good mechanical resistance the TEOS/copolymer solution was deposited on inorganic supports via spin-coating. Preliminary experiments, carried out using mica as support, allowed the optimization of the synthesis and the characterization of the material. Afterwards the film was deposited on permeable supports, Si_3N_4 macrosieves (pores 0.45-5 μm), and tested. The final composite membrane showed an homogeneous silica top layer covering the Si_3N_4 support (Fig. 1A). In principle the silica nanopores are tunable in size; in addition to size selectivity, the final aim of the device is to tune the diffusion of molecules applying an external stimulus (for instance, pH variation, ionic strength modification etc.). The microfluidic device (Fig. 1B) was constituted by two half-cells in Pyrex physically separated by the porous membrane, fixed using two silicone seals covered with teflon. Preliminary diffusion tests with molecules with different sizes (phenol, chlorophenols and dyes) in the presence of only Si_3N_4 microsieves checked the applicability limits of the system. In addition TOC analysis excluded the release of organic impurities from every part of the device. Then the study focused on a cationic dye: methylene blue. The system allows the selective passage through the porous membrane of different types of molecules on the basis of their sizes, polarity and charge. In the case of charged species the passage can be favoured by a potential difference at the two sides of the membrane, obtained by the application of an electric field.

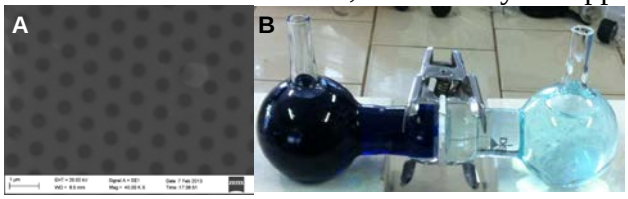

Fig. 1. A) SEM image of silica porous film deposited on Si_3N_4 macrosieves. B) Microfluidic device.

P65 - DETERMINATION OF CAFFEINE @ GOLD NANOPARTICLES MODIFIED GOLD (AU) ELECTRODE: A PRELIMINARY STUDY

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Caffeine (1,3,7-trimethylxanthine) is a natural alkaloid exerting many physiological effects, such as stimulation of the central nervous system, diuresis and gastric acid secretion. It is widely distributed in plant products and beverages [1] and its quantification is mainly of pharmaceutical and alimentary concern. Many methods, including spectrophotometry, chromatography and biosensing [2,3] were proposed to this aim. Usually, these methods are generally more expensive, time-consuming and complicated than electroanalytical ones [3]. However, the major drawback of the electrochemical determination of caffeine at the more common electrode materials (e.g., metals, glassy carbon) is that its oxidation occurs at a very positive potential, thus overlapping with the discharge of the background medium [3], generally not exactly reproducible.
In this paper, we describe a method based on the modification of a gold electrode (Au) surface by deposition of functionalized gold nanoparticles. Preliminary cyclic voltammetric experiments were performed to study the caffeine voltammetric behavior at Au modified electrode. As previously reported [3], the oxidation system is characterized by an anodic peak in the positive-going step and by the absence of any cathodic peak on the reverse scan, indicating that the oxidation is irreversible**.** At the modified electrode, the voltammetric peak height increases vs that @ the bare one, depending on the nanoparticles functionalization. The best performances were observed @ Au electrode modified with colloidal gold nanoparticles (AuNPs) stabilized into a chitosan matrix . Differential pulse voltammetry (DPV) was used to perform electrochemical measurements due to its high sensitivity and predominant separation from background current. Analytical parameters such as reproducibility, interference rejection, response time, storage and operational stability of the caffeine sensor have been investigated.

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P66 - INFLUENCE OF DIFFERENT BIOLOGICAL ENVIRONMENTS ON THE STABILITY OF SEROTONIN DETECTION ON GOLD NANOPARTICLES MODIFIED SCREEN PRINTED ELECTRODES

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Serotonin (5-HT) is an important neurotransmitter that plays important biological roles in various areas of the body. 5-HT is known to influence key neurological traits, such as anxiety [1], but also plays a key role in driving gastrointestinal motility and platelet aggregation
Serotonin (5-HT) is a key neurotransmitter that is found in the brain, blood and gastrointestinal tract. Due to the interest in measuring this important biogenic amine in these various environments, measurements have been conducted without understanding the influence of the matrix on the stability of recordings.
Electrochemical recordings were carried out in PBS buffer, 0.5% w/v mucin and 5% w/v albumin on gold Screen Printed Electrodes (AuSPEs) and on gold nanoparticles modified AuSPEs. During recordings of 5-HT on AuSPEs, the 5% w/v albumin matrix was protective against electrode fouling compared to 0.5% w/v mucin, which enhanced the rate of electrode fouling. On AuNPs modified AuSPEs, 0.5% w/v mucin once again enhanced the rate of electrode fouling, however 5% w/v albumin did not alter the rate of fouling compared to PBS buffer. This data suggests that all proteins cannot be considered to behave in a similar fashion for electroanalytical measurements and thus careful consideration on the matrix effect needs to be considered before biological monitoring. Measurements in various matrices are becoming more common with the widely applicability of biological monitoring. For the continuous monitoring of 5-HT using SPE, 5% w/v albumin in PBS was shown to act in a protective fashion, whilst 0.5% w/v mucin in PBS was detrimental to the observed response. However using AuNps modified AuSPE to monitor 5-HT the presence of the two different proteins in albumin and mucin did not alter the degree of electrode fouling. Other than the mucin, matrix AuNPs modified SPEs was more stable in all other matrices compared to AuSPEs.

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P67 - BIOMIMETIC SORBENTS AS SPE STATIONARY PHASE FOR THE DETERMINATION OF CANNABINOIDS BY LC-MS/MS.

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Sample preparation is a critical step in bioanalytical methods and is a key factor in determining the success of analysis. Conventionally, liquid–liquid extraction (LLE), protein precipitation (PP) and solid-phase extraction (SPE) are used as sample preparation techniques. Traditional SPE sorbents range from reverse phases to ion-exchange and polymeric materials. In the past decade specific affinity-based stationary phases have been developed; biomimetic ligands such as MIP [1], aptamers [2] and peptides have been recently proposed as alternative candidates to antibodies. Only a few examples of peptides used as SPE stationary phases have been reported to date [3]: peptide ligands are able to specifically interact with molecules, similarly to enzymes or receptors and possess some interesting characteristics such as low costs, rapid synthesis and stability. The design of the amino acid sequence is very important to obtain a ligand with good affinity and selectivity for the target molecule. Modern computational tools have greatly improved the rational design of the peptide libraries, significantly reducing the huge number of possible candidates to synthesize, obtained by combinatorial approaches. The aim of this work was the development of novel SPE stationary phases constituted by peptide ligands for the determination of cannabinoids in various biological matrices. Firstly a set of hexapeptides targeting cannabinoids has been identified using molecular modeling software and searching algorithms traditionally applied in drug design. The designed peptides were synthesized and then packed on SPE cartridges. The better SPE conditions were tested in model solution and then in matrix, through the optimization of different parameters such as pH, nature of extracting solvent etc.

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P68 - THE INTERNATIONAL POLY IMPLANT PROTHÈSE (PIP) IMPLANTS SCANDAL: ANALYTICAL INVESTIGATIONS

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In 2010, the French health authority was the first to ban the use of implants from Poly Implant Prothèse (PIP). It has been estimated that a huge number of these adulterated implants have been implanted into hundreds of thousands of unknowing women around the world (around 500.000), from Europe to South America. They were fraudulently manufactured with substandard, non-medical grade silicone, and recent clinical studies consistently confirmed their significant higher rupture rate, migration to axillary lymph nodes and incidence of silicone locoregional spread compared to implants from other manufacturers [1,2]. To date, fifteen thousands French women have been explanted. Aim of our recent ongoing studies [3] is to understand on analytical grounds the reasons of the exceptional rupture rate of these implants and whether there are potential relevant toxicological consequences from the exposure of human body to the silicones present in their composition unapproved for medical applications.The study was conducted on filler silicone and elastomeric shells from (i) non implanted intact PIP breast prostheses, (ii) PIP implants from n=3 patients explanted for therapeutical reasons (capsular contraction), (iii) late periprosthetic fluids (LPF) from n=4 patients with ruptured PIP implants. Further informations were obtained by comparison of the results with those from a virgin Mc Ghan 410 MX prosthesis and from a sample of technical-grade non-cohesive silicone.The specimens were analysed using rheological techniques, attenuated total reflectance infrared spectroscopy (ATR-FT-IR), nuclear magnetic resonance (^{1}H NMR), gas chromatography coupled to mass spectrometry (GC–MS), high performance liquid chromatography (HPLC-UV-DAD) and flow injection electrospray mass spectrometry (FI-ESI-MS). Filler silicones, elastomeric shells and LPF were also submitted to phase contrast microscopy to investigate their morphological characteristics. Our results indicate that the higher rupture rated of PIP implants are due to the combinations of different factors involving both the elastomeric shell and filler silicone (and LPF):(i) the presence of extraneous non silicone residuals (2-hydroxy-isobutyrophenone, 2,2-diethoxyacetophenone and biphenyl-4-carboxaldehyde), known as UV sensitive radical initiators may elicit the inflammatory reactions that accelerate capsular formation and contracture; (ii) the consequent mechanical stress enhances silicone bleeding and rupture of the weak elastomeric shell; (iii) the non cohesive (as demonstrated by comparison of its properties with those of an approved implant [3]) filler silicone is incorporated by emulsification into the surrounding LPF. Finally, the exposure of this silicone/LPF microemulsion to the draining breast lymphatic system, leads to its irreversible active migration and accumulation to axillary, neck and infra-thoracic mediastinal lymph nodes, thus to evolve to the severe siliconomas formation and inflammatory reactions often diagnosed in the patients carrying this faulty, adulterated product.

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P69 - DYES AND REACH REGULATION: AN ANALYTICAL APPROACH

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The Candidate List of substances in articles (REACH Regulation, EC 1907/2006) includes chemicals that are defined as substances of very high concern (SVHC) on the basis of their toxicity and ecotoxicity. Recently, four triarylmethane dyes have been included in the Candidate List in view of the possible presence of Michler's ketone and Michler's base as specific impurities in concentrations higher than 0.1% in the substance. Moreover, REACH Regulation confirms the “restrictions” of EU Directive 2002/61/EC regarding the release of aromatic amines from all azo dyes and from articles that contain these organic colorants.
Thus, the current regulation requires a more accurate characterization of the imported substances by UE manufactories, also considering that dyes are now mainly produced in far-east countries and imported in EU as raw substances. Similarly, detailed controls have to be implemented on the related industrial products, i.e. both the mixtures of dyes manufactured by EU companies and the final articles in which they are contained.
In this connection, the analytical procedures for the complete chemical characterization of dyes should be revised, optimized and possibly transferred to the manufactures for a systematic control of both imported substances and final products. Actually, this objective is often hindered by i) the absence of validated analytical methods, ii) the lack of analytical standards and iii) the difficulties in the accurate determination of the chemical structure of the molecules of interest (dyes and impurities) [1].
In this presentation, the analytical approach adopted by the analytical chemistry group of University of Padova, in collaboration with two Italian dyes manufactures, for the correct characterization of organic dyes in view of their REACH registration or CLP notification is reported. It is based on the integrated acquisition of instrumental analytical data (mainly HPLC-DAD, HPLC-MS, GC-MS, ^{1}H-NMR e ^{13}C-NMR) for a compete qualitative (including structural) and quantitative analysis of these substances.

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P70 - CHARACTERIZATION OF NANOSILVER TEXTILES AND EVALUATION OF AG RELEASE AND PERCUTANEOUS ABSORPTION: AN IN VITRO STUDY

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An *in vitro* experiment by means of a Franz diffusion cell apparatus was performed in order to evaluate the percutaneous absorption of silver released by biomedical textiles containing silver nanoparticles. Two different kinds of wound dressings and a pajama for children affected by atopic dermatitis have been characterized with Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) before a release test in synthetic sweat. After 24 hour of soaking all the materials showed silver chloride clusters (revealed by SEM analysis) on the surface and silver was revealed in the bathing solution by means of Graphite Furnace Atomic Absorption Spectrometer (GF-AAS) in a range of concentration from 40 to 100 µg/g (w/w). Once evaluated silver release, an experiment with Franz diffusion cells for each material tested revealed silver permeation through human skin only after 20 hour. At 24 hour silver retained inside skin samples was quantified by means of Inductively Coupled Plasma Mass Spectrometer (ICP-MS). SEM analysis of skin samples showed the presence of silver aggregates both in epidermis and dermis. Because of the large dimension of the silver-silver chloride aggregates it is possible to hypothesize that precipitation phenomena occur through the skin layers [1]. These results allow predicting the possibility of systemic absorption of silver in case of a prolonged use of these devices (since dermis is vascularized) depending also on the integrity of the skin treated: deposition of nanoparticles through the skin layers is moreover relevant in case of burns and damaged skin as reported by Rigo et al. (2012) [2].

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P71 - PRESSURIZED LIQUID EXTRACTION FOR THE EXTRACTION OF CANNABINOIDS AND METABOLITES FROM HAIR: DETECTION OF CUT-OFF VALUES BY LC-MS/MS

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Hair analysis has become a routine procedure in most forensic laboratories since this alternative matrix presents some advantages compared to classical ones such as the longer time window, the non-invasive sampling and the stability [1]. Nevertheless cannabinoids analysis in hair keeps being not straightforward because of the low concentrations of THC and its major metabolite 11-nor-9-carboxy-THC (THC-COOH) that is even less concentrated (fg/mg) [2]. The determination of THC-COOH is crucial to distinguish between passive drug exposure and active consumption. To date the only technique able to reach the cut-off of 0.2 pg/mg recommended by SoHT for THC-COOH determination is gas chromatography coupled with tandem mass spectrometry. Liquid chromatography coupled with mass spectrometry (LC–MS/MS) has been used in cannabinoids hair analysis just in a few works; THC-COOH was included only in one study [3] but the LOQ obtained is higher than the cut-off. Sample preparation is almost exclusively based on alkaline digestion generally followed by liquid liquid extraction, however analytes stability might be affected during the digestion.
The aim of the present work was to develop a fast and accurate method for the determination of cannabinoids and metabolites in hair. The extraction of analytes from hair is based on an automated pressurized liquid extraction (PLE) using as eluent phase water modified with sodium dodecyl sulphate. The PLE eluent is then cleaned-up by SPE that allowed both the reduction of matrix effect and the concentration of the analytes which is particularly useful for the detection of THC-COOH. The whole procedure has been validated according to SOFT/AAFS guidelines. 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 cut-off values.

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P72 - NIR SPECTROSCOPY AND CHEMOMETRICS IN FORENSIC CHEMISTRY: AKB48 DETERMINATION.

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Near infrared spectroscopy (NIR) followed by chemometrics is an always more useful tool for the characterization and the determination of analytes in complex matrices of different fields (food, environment, pharmaceutics, etc) [1-3]. In forensic chemistry, this approach has been successfully applied in several applications [4-5].
In this work, the determination of AKB48 (*N-(1-Adamantyl)-1-pentyl-1H-indazole-3-carboxamide)*, a new synthetic cannabinoid not included in the list of illicit drug of abuse, has been evaluated in cooperation with the italian scientific police (RIS) of Roma.
Several different vegetal matrices were prepared in the laboratory, to simulate real illicit drugs of abuse. The application of the NIR spectroscopy analysis followed by chemometrics shows that it is possible to determine the presence of the AKB48 in real complex matrices.
These results confirm that NIR spectroscopy is a fast, cost-effective and useful tool for the preliminary determination of synthetic cannabinoids in forensic science.

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P73 - A CONGENER APPROACH TO TOTAL POLYCHLORO-BIPHENYLS DETERMINATION

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Polychlorinated biphenyls (PCBs) exist as 209 congeners according to the number and position of chlorine atoms, and their mixtures known by the trade name Aroclor, were manufactured from 1929 to 1979 for commercial use and broadly distributed. Levels of PCBs in air, soil, water and biota are routinely determined in samples from around the globe. Their pervasive nature and prevalence studies indicated that PCBs were the epitome of persistent organic pollutants (POPs) [1]. The complexity of the problem regarding industrial prevalence, environmental distribution and accumulation requires an effort to continue the path to more effective regulation and accurate analytical determination of PCBs is key to ensure an effective environmental management [2]. Often analysts have to deal with the question of determining the total concentration of PCBs. The complexity of different industrial mixtures used and the high number of possible congeners make the issue a challenge still open for analytical laboratories. The analysis of environmental samples has been usually faced with the Aroclor fingerprinting approach [3]. The method requires a quantitation based on the empirical identification of the Aroclor mixture by the analyst via visual inspection of the chromatogram. However the reliability of the identification is questionable and the frequent occurrence of more than one Aroclor mixture in the sample and weathering processes complicate pattern matching. This can produce biased quantitations and non homogeneous data from different laboratories [4]. Our alternative approach is based on the determination of 13 congeners, which represent the most significant in environmental and toxicological fields. The pattern of relative abundances of this defined number of congeners is mixture-specific and allows objective criteria for Aroclor identification. A quantitative relationship between Aroclor concentration and the sum concentration of the 13 congeners is established for any single mixture or mixtures combination. The fundamental advantage of this approach is that identification and subsequent quantitation are based on definite criteria. This reduces significantly the possibility of biased quantitations due to incorrect identifications. Moreover our congener based approach allows the use of GC/MS techniques in addition to classical ECD for Aroclor quantitation improving selectivity and detection capabilities. In environmental forensic investigations the differences in the pattern of relative congener abundances can be used as fingerprint of different Aroclors and mixture of Aroclors, including weathering effects, aimed to understand the source and fate of PCBs contamination.

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P74 - SEVERAL KINDS OF SKIN INFLUENCE IN VITRO METAL NANOPARTICLES PERMEATION

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Metal nanoparticles (MNPs) production is increasing because of their wide range of application. Due their antimicrobial activity, silver NPs are largely used in biomedical devices (such as wound dressing or surgical prosthesis) as well as in textiles or products of common use that provide a close contact with skin; so dermal exposure and uptake is being debated as an important uptake route for AgNPs [1]. This study aims to compare different protocols of skin sample storage in the measurement of AgNPs dermal permeation.
Three samples of human skin with different degrees of cell viability und structural integrity (fresh skin: 100% cell viability and integrity; cryopreserved skin: 50% cell viability and good structural integrity; glycerolated skin: 0% cell viability and high fragility of the stratum corneum) were tested by means of a Franz diffusion cell apparatus to evaluate AgNPs percutaneous absorption [2]. An average of eight Franz cells were used for cryopreserved and fresh skin, while five cells were used for glycerolated skin. Donor chambers were filled with a suspension of AgNPs (20nm) in synthetic sweat and receptor compartments were filled with physiological solution (at 32°C). At selected intervals of time 1.5 ml of the dermal bathing solution were removed and analyzed by means of ICP-MS. At 24 hour of experiment silver skin content was evaluated after mineralization of skin samples in nitric acid. Silver revealed during the range 2-24 hours in the receiver phases of cells loaded with glycerolated skin was significantly higher than of that revealed in cells loaded with cryopreserved and fresh skin. The silver content measured in cryopreserved skin was significantly higher than in glycerolated and fresh skin.
These results confirm that: (i) skin permeation pathways differ according to the characteristics of vitality of the skin used in in vitro studies; (ii) AgNPs in commercial formulations and medical devices should take into account the purposes for which it is intended their use.

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P75 - CHEMICAL FRACTIONATION OF Cd, Pb AND Cu IN ANTARCTIC AEROSOL BY SEQUENTIAL EXTRACTION (WATER-SOLUBLE, ACID EXTRACTABLE AND INERT FRACTIONS) AND SWASV DETERMINATION

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Continuing from a previous project [1,2], a three-step sequential extraction procedure for the determination of the water-soluble (below, simply soluble), dilute-HCl-extractable (below, extractable) and inert fractions of Cd, Pb and Cu in atmospheric aerosol was set up and applied for studies in Antarctica. Eight PM10 aerosol samples were collected in the vicinity of the "M. Zucchelli" Italian Station during the 2000/01 austral summer using a high-volume sampler and pre-cleaned cellulose filters. The aerosol mass was determined by differential weighing of filters carried out in the clean chemistry laboratory of the station, under controlled temperature and humidity. Metals were determined by an ultrasensitive square wave anodic stripping voltammetric procedure (SWASV). Additivity of the three fractions to give the total metal content was tested and verified.

Particulate metal concentrations ranged as follows: Cd 1.4–38 μg/g (average 11.2 μg/g), Pb 25.3–83 μg/g (average 47 μg/g), Cu 150–840 μg/g (average 493 μg/g). In terms of atmospheric concentration, the values were: Cd 0.95–39 pg/m^3 (average 10.3 pg/m^3), Pb 17.1–60 pg/m^3 (average 33 pg/m^3), Cu 89–430 pg/m^3 (average 344 pg/m^3).

The chemical fractionations of the three metals and their seasonal distributions (referring to the particulate composition) are as follows. The extractable fraction predominates in the first part of the season, with maxima at mid-December for Cd (8.8 μg/g, 96%) and Pb (81 μg/g, 98%), and mid-January for Cu (421 μg/g, 56%). The soluble fraction predominates late in the season, with maxima at mid-January for Cd (3.3 μg/g, 59%), the end of January for Pb (16.8 μg/g, 55%) and in February for Cu (280 μg/g, 43%). The inert fraction shows quite different behaviours between Cd, on one side, and Pb and Cu, on the other. For Cd it peaks in the middle of the season, with a maximum of 32 μg/g (84%) at the end of December. For Pb and Cu the inert fraction fluctuates considerably during the summer, with high correlation for the two metals (r=0.9707) and maxima at the beginning of December (Pb 37 μg/g, 60%, and Cu 268 μg/g, 32%) and in February (Pb 23 μg/g, 63%, and Cu 217 μg/g, 33%). Interpretation of chemical fractionation data will be presented in terms of major sources of aerosol material in Antarctica.

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P76 - POLYBROMINATED DIPHENIL ETHERS (PBDES) DETECTION USING GC-MS, ELISA AND AN ELECTROCHEMICAL MULTIPLEXED BIOSENSOR

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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 in the air, water, food due to their low reactivity, high hidrophobicity and bioaccumulative properties causes a continuous exposure to these compounds. Moreover PBDEs are known to cause severe health problems and thus the commercially available mixtures have been banned from the market.
The objectives of this study were to provide updated measurements of PBDEs in food by GC-MS analysis, to estimate possible difference in levels from differing types of food samples and to afford an improved estimate of current dietary intake. Moreover, the suitability of using a magnetic particle enzyme-linked immunoassay (ELISA) to analyze PBDEs in food samples was also tested. Moreover, an electrochemical multiplexed biosensor for the simultaneous detection of PBDEs and PCBs (polychlorinated biphenyls) was also developed. Food samples were randomly acquired in breeding farm and slaughterhouse. Samples were ASE extracted, cleaned up on a Power-Prep system and finally analyzed.

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P77 - PCB-11 IN ANTARCTIC LAKES AND SNOW

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Antarctica is usually considered a pristine ecosystem, nevertheless it is influenced by persistent organic pollution, mainly due to a cold-trapping process driven by the long range atmospheric transport. Polychlorinated Biphenyls (PCBs) were detected in the Antarctic environment since decades ago. In the last few years there has been an increasing interest about the congener 3,3'-dichlorobiphenyl (PCB-11). This was almost absent in original Aroclor mixtures but it largely derives from consumer goods containing azo- and phthalocyanine pigments. Recently it has been found as a contaminant in various environments worldwide [1] and even in Antarctica [2, and ref. therein], where it represented one of the most abundant congeners. In this work we focus on the determination of PCB-11 in lake water and superficial snow samples collected in Northern Victoria Land during the 27th Italian Antarctic Expedition (austral summer 2011–2012). Six summer ice-free lakes near Terra Nova Bay (Carezza, Edmonson Point 15A, Edmonson Point 14, Tarn Flat 20, Inexpressible island 10B, Gondwana) were investigated, together with five snow-covered sites (David Glacier, Vegetation Island, Mid Point, ITASE GV5, Campo Faraglione) ranging from coastal areas to East Antarctic plateau. Samples were collected in pre-cleaned airtight stainless steel containers, allowed to melt and continuous liquid-liquid extracted at the Mario Zucchelli Station in Antarctica. Afterwards extracts were purified onto a disposable neutral silica column with an automated system (PowerPrep™, FMS) and analysed by HRGC-HRMS (HP 6890 - MAT 95XP Thermo Finnigan). Quantification was performed using internal standards and isotope dilution technique. Results were corrected using procedural blanks.
PCB-11 was detected in all the samples, with comparable levels in each lake (few pgL^{-1}); slightly higher values were found in snow samples, maybe because of the larger surface area.
Funds were provided by PNRA 2009/A2.10.

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P78 - POLYCYCLIC AROMATIC HYDROCARBONS IN ORANGE LEAVES IN SEVILLE (SPAIN): AN INDICATOR OF URBAN AIR CONTAMINATION LEVEL

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Polycyclic aromatic hydrocarbons (PAHs) are considered important environmental contaminants because of widespread occurrence, strong persistence, long-range transportation potential, and toxicity to organisms. One of the main sources of PAH emissions in urban areas is represents by traffic since these substances are produced during incomplete fuel combustion. In areas less affected by traffic an important source is represented by wood and grass burning. The classical way to monitor PAHs in the atmosphere is to use active air sampling techniques which are often expensive. PAHs may accumulate in vegetation due to contaminant affinity for lipids present in the leaves although plants can also sequester PAHs from soil through roots. Therefore vegetation can be used as a passive sampler to indicate contamination levels of PAHs in local air.

Leaves samples of orange trees were collected in Seville from roadside of ten streets with heavy traffic (5 with high and 5 with low traffic) and inside three city parks, in order to measure polycyclic aromatic hydrocarbons (PAHs) concentrations. An analytical method suitable for the determination of PAHs was developed and optimized, using solid-phase extraction (SPE) and High Performance Liquid Chromatography (HPLC). In general, as expected, samples collected at roadsides were characterized by higher concentrations of PAHs (1071 μg/Kg for the five streets with more traffic and 1028 μg/Kg for the five streets with lower traffic) with respects the three parks (on average 363 μg/Kg). For some specific congeners (i.e. benzo[ghi]perylene) higher concentrations were encountered for three sites, including one of the parks, indicating probably the presence of specific local sources. The data have been also submitted to a multivariate data treatment by PCA and HCA. PAH diagnostic ratios were also estimated to discriminate among possible sources.

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P79 - METALS IN ATMOSPHERIC AEROSOL FROM URBAN AND MARINE SITES IN ITALY: A COMPARISON BETWEEN PIXE AND ICP-AES MEASUREMENTS

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PIXE (Particle Induced X-ray Emission) and ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) techniques are largely used in atmospheric aerosol studies. PIXE allows carrying out an elemental analysis of the particulate without any solubilization, thus reducing the analysis time and the contamination risk [1]. Conversely, ICP-AES data depend on the extraction conditions such as extracting solution composition, pH, temperature and contact time. Whereas PIXE is able to provide the total concentration of the elements, ICP-AES data refer to the amount available in the extraction conditions, which can mimick the ones of natural systems. Hence, ICP-AES measurements represent an efficient tool to better evaluate the impact of heavy metals on the environment and the human health.
We present here a comparison of parallel PIXE and ICP-AES measurements of Fe, Al, Cu, Pb, Mn, Cr, Ni, V, As performed on PM10 and PM2.5 samples. Two extraction procedures were applied to samples from 5 sites at different anthropization level in Italy: a "soft" extraction (HNO_3 at pH= 1.5 in ultrasonic bath at room temperature) and a "strong" extraction (micro-wave oven in HNO_3 and H_2O_2), following the procedure reported in the EU regulation (EN 14902 2005).
The extent of the metal extracted in the different conditions resulted to be strongly dependent on the sampling site, on the main sources of the particle containing the metal (crustal or anthropic) and on the sampled size class (PM2.5 and PM10) [2]. In soft extraction conditions, metals mainly arising from anthropic source showed a higher solubility than the crustal ones. When PM10 and PM2.5 was sampled in the same site, metals in PM2.5 showed a higher soluble fraction, due to the dominance of anthropic sources. The "strong" extraction with HNO_3 and H_2O_2 was found to solubilize almost all the metals in the PM2.5 in sites with different contribution of anthropic and natural sources.

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[2] R. Traversi, S. Becagli, G. Calzolai, M. Chiari, M. Giannoni, F. Lucarelli, S. Nava, F. Rugi, M. Severi, R. Udisti. Nucl. Instr. & Meth. B (2013) accepted.

P80 - HUMIC SUBSTANCES DISTRIBUTION IN ANTARCTIC COASTAL MARINE SEDIMENTS (ROSS SEA ANTARCTICA)

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In order to understand the global carbon cycle particular attention must be paid to sedimentary organic matter (OM) because of it is the major reservoir of organic carbon. Marine organic matter is mainly composed by material derived from the various plankton species including primary producers and consumers in overlying surface waters. In antarctic continental shelf regions allochthonous materials can be introduced by means coastal erosion by melting ice. Only a fraction of the organic material that is produced within the photic zone reaches the sea floor. Organic matter degradation due to aerobic and anaerobic remineralisation processes could hence occur within the sediment. During the last few decades many researcher have highlighted that preservation is highly selective, and that the amount and composition of OM preserved in marine sediments could change greatly among regions and depositional environments [1].
In this context, the knowledge of the formation/degradation processes of humic substance within the sediment assumes a significant relevance since humic substances are known as main constituents of sedimentary organic matter. Moreover, the importance of the knowledge of humic substance in aquatic ecosystems consists of the great complexing ability of humic and fulvic acids, which is attributed to the different oxygen-containing functional groups, such as carboxylic, phenolic and carbonyl groups.
During different Antarctic oceanographic cruises surface sediments (0-10 cm) were sampled, and humic material was analysed. In this paper, is discussed the distribution of humic substance along the Ross Sea continental shelf costal area. The amount of humic substance has been correlated to sediment accumulation rate. The results showed the great influence of terrestrial input in this area. Analytical characterization of extracted humic substances confirmed these results [2].

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[2] N. Calace, M. Pietroletti, B.M. Petronio, M. Scarpiniti, M. Mecozzi, Int. J. Environment and Health, 5 (2011) 246-261

P81 - EVALUATION OF TOXIC METALS BIOACCESSIBILITY IN URBAN SOILS.

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Soils represent an important sink for lots of contaminants, including metals, organic pollutants and many other potentially dangerous substances. Urban soils, in particular, can often be characterized by high levels of metals (due to industrial activities, vehicular traffic, etc.), implying significant health risks for organisms exposed to them, including humans. For young children, incidental ingestion of soil and dust, via hand-to-mouth activity, represents the principal direct pathway for exposure to non-dietary sources of metals in contaminated areas. Also activities like gardening (in which children are often encouraged to participate in) and cultivation can increase humans' contact with contaminants in soils, therefore the health risks need to be clearly understood. It is generally known that the total concentration of metals (and, in general, of pollutants) is not a good indicator of their health risk, the extent of harmful effects being strongly dependent on the availability to target organisms. The amount of a pollutant that can be absorbed by a target organism that is exposed to it can be defined as its bioavailable fraction, whose determination is primary to accurately quantify metal exposure via soil ingestion. Since the impossibility in the direct use of humans in bioavailability experiments, the most accurate results can be obtained using immature swine as a surrogate model, because of their similarities to man in metabolism, nutritional requirements, bone development, and so on (*in vivo* tests). However, given the time and cost requirements, in addition to ethical issues, this procedure is quite difficult to apply. A good compromise can be the measurement of bioaccessibility instead of bioavailability, defining the bioaccessible fraction of a contaminant as its maximum amount potentially absorbable by a target organism. To this end, simple, rapid and inexpensive procedures seem to be *in vitro tests* (e.g., SBRC, IVG, PBET, DIN).
The aim of this work is first to compare and optimize two of the most used *in vitro tests* (SBRC and IVG) and subsequently to evaluate human bioaccessibility of toxic metal in urban soils. To this end, the mentioned procedures have been applied to some soil samples, characterized by different levels of metal contamination, and their performances and results compared. The comparison indicated that the SBRC *in vitro test* was simpler, faster and more reliable. The results obtained applying the optimized procedure to six garden soils samples, collected in Genova, are presented and discussed.

P82 - APEX (AQUEOUS PHOTOCHEMISTRY OF ENVIRONMENTALLY OCCURRING XENOBIOTICS): A NOVEL SOFTWARE TOOL TO PREDICT THE PHOTODEGRADATION OF ORGANIC POLLUTANTS IN SURFACE WATERS

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Photochemical processes play an important role in the transformation of organic pollutants (including pesticides) in surface waters. They are usually divided into direct and indirect photolysis: in the former case, absorption of sunlight by the pollutant triggers a transformation reaction. In indirect photolysis, sunlight-absorbing molecules (*e.g.* chromophoric dissolved organic matter -CDOM-, nitrate and nitrite) produce reactive transients including $^{\bullet}OH$, $^{1}O_2$, CDOM triplet states ($^{3}CDOM^*$) and $CO_3^{-\bullet}$ [1]. The rate and, therefore, the importance of photochemical reactions depend on several features of both the environment and the pollutant, such as sunlight irradiance, water depth, chemical composition and absorption spectrum, and on pollutant photochemical reactivity (direct photolysis quantum yield and reaction rate constants with $^{\bullet}OH$, $^{1}O_2$, $^{3}CDOM^*$ and $CO_3^{-\bullet}$) [2]. We have recently developed a photochemical model to predict pollutant phototransformation kinetics as a function of water chemistry and depth, based on photochemical reactivity parameters of the pollutant. The model has been validated towards the degradation of several xenobiotics in surface-water environments, including pesticides [3-5]. Built on such basis, the APEX software predicts pollutant photodegradation kinetics, steady-state concentrations of photoreactive transients, and formation kinetics and yields of intermediates. Needed input data for APEX are direct photolysis quantum yields, reaction rate constants with $^{\bullet}OH$, $^{1}O_2$, $^{3}CDOM^*$ and $CO_3^{-\bullet}$, and intermediate formation yields *via* each process. The experimental protocol to derive such data has been described in detail in several publications [3-5].
The APEX code is based on the open software Octave (http://www.gnu.org/software/octave) and it is available for free download at http://chimica.campusnet.unito.it/do/didattica.pl/Quest?corso=7a3d.

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P83 - MAJOR AND TRACE ELEMENTS AND REEs CONCENTRATION IN AEROSOL SAMPLES COLLECTED AT NY-ALESUND (SVALBARD ISLANDS) DURING THE 2010 CAMPAIGN.

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Aerosols and their interactions with clouds and the surface can have a significant impact on the radiative balance in the Arctic. This holds true especially for the spring season when the Arctic environment is climatologically very sensitive and intrusion of air masses with a high aerosol load from northern continental regions is favoured. In particular, the atmospheric transport from the highly industrialized areas at mid latitudes of the northern hemisphere represents a major delivery pathway of trace metals as well as ionic species to the remote Arctic environment.
At the purpose of achieving a better knowledge of the timing and impact of such processes, a continuous aerosol sampling during spring and summer seasons was carried out at Ny-Alesund (Svalbard Islands) using a PM10 sampler (24 h resolution) with Teflon filters, for ions and metal determination.
In order to obtain a complete chemical characterization of the collected PM10 samples, Ion Chromatography (IC) and ICP-SFMS were applied. In particular, in order to improve the sensitivity of the ICP-SFMS technique, an APEX desolvatation system, equipped with an ACM module able to reduce the oxide interferences has been employed in sample introduction system. Such a system set-up in this work has made possible the quantification of sub-ppb level analytes.
The temporal evolution of the atmospheric concentration of selected elements during the 2010 sampling campaign is here presented. Moreover, the identification of specific transport events (long range or local), sea spray, dust and biogenic contributes along the whole campaign are here reported. Finally, the identification of the main source areas of the crustal dust reaching the sampling site at Ny-Alesund and their relative contributions in different periods was attempted using different approaches (e.g. by studying the LREE/HREE - Light Rare Earth's Elements/Heavy Rare Earth's Elements – ratio).

P84 - SOURCE APPORTIONMENT OF AEROSOL PARTICLES AT THE ARCTIC SITE OF NY ALESUND (SVALBARD ISLANDS) BY PMF ANALYSIS.

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The global climatic change has been primarily attributed to anthropogenic emissions of carbon dioxide. However, the temperature in the Arctic has increased at a rate twice as high as the rest of the world [1], which has been partly explained by the surface forcing and surface temperature response of pollutants including methane, tropospheric ozone and aerosol. Investigations over the past decades have shown that a considerable part of the Arctic troposphere is significantly influenced by atmospheric pollution of distant latitude origin. In order to quantify the natural and anthropic sources of atmospheric particles at Ny-Ålesund, (78.9°N, 11.9°E, Svalbard Islands) the results of Positive Matrix Factorization (PMF) applied on PM10 chemical data are here reported. Aerosol sampling was carried out using a PM10 samplers with Teflon filters at 24h resolution from March to September 2010. Analysis was performed by ion chromatography for ion composition, and ICP-SFMS, for selected metals and Rare Earth's Elements; both techniques are optimized [2] in order to be sufficiently sensitive, accurate and reproducible to be applied to very low atmospheric load of aerosol particles, typical of remote polar regions.
Preliminary results show that six sources were sufficient in a PMF analysis to account for the sources contributing to the aerosols load at Ny Alesund, including a primary marine source, a secondary biogenic, a secondary long range, Nitrate and two crustal source, one more related to local contribution and another long range transported (characterized by higher ratio Light Rare Earth's Elements/Heavy Rare Earth's Elements).
Cluster backward trajectories analysis show that at Ny Alesund the air masses from North Russia and North Europe (Norway, Sweden, Finland) prevail in spring while the Arctic Ocean and local soil source contribution is dominant in summertime.

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P85 - ANALYTICAL ROUTE FOR HYDROGEOLOGICAL ANOMALIES: THE CASE OF A "WHITE" SPRING IN MINE VALLEY (LIVIGNO – ITALY)

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The Livigno area represents a good test for the groundwater system reconstruction in the mountain environment because it has a complex geological and tectonical setting. In order to characterize this aquifer, a multidisciplinary approach, based on lithological, geochemical, hydro-geological and geo-structural methods, has been adopted.
The Livigno area is located at 1800 m s.l.m. in the central Alps (northern Lombardy – Italy). For the tectonic setting this area is comprise between the Err Bernina system (Lower Australpine) and the Ortles-Quatervals system (Upper Austroalpine). The most important regional fault is represented by Zebrù fault. This fault divides the sedimentary rocks constituted by Fraele and Monte Motto limestone (Lias) to crystalline basement, which is constituted by "Bormio phyllades" and "Punta Rossa Formation". To the north of Zebru fault system the Alpisella fault system outcrops and divides the Monte Motto limestone by Triassic dolomites and limestones.
In the Livigno area 32 springs were sampled and analyzed. In particular, in the Mine Valley (in the south part of the Livigno area) there is a peculiar spring, named "White", which shows a peculiar unknown whitish deposition.
The first step was to characterize that compound through the integration of several analytical techniques: XRD, SEM-EDX, FTIR, ICP-MS. Using this approach we tried to have a complete picture of the problem, also matching results with hydro-geochemical information. Via the elemental analysis with EDX was identified the presence of aluminum, sulfur, oxygen and silicon.
Subsequent analysis and bibliographic documentations [1] allowed us to identify the following structure tridecameric of $Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SO_4)_4 \times 13H_2O$, and detect an anomaly in the presence of rare earth elements (REE) in the whitish compound.
The second step was to analyze closely at Livigno water, which confirmed this peculiarity in REE in the "White" spring.

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P86 - pH-STAT LEACHING TEST AUTOMATIC APPARATUS DEVELOPMENT TO CHARACTERIZE GRANULAR WASTE.

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The hazardous potential of solid waste depends both on pollutants content and on pollutants mobility. The contaminants mobility is a key parameter that is investigated by leaching tests. Among many parameters which control the release of contaminants from waste in the environment, pH is one of more effective. pHstat leaching test, defined by CEN/TS 14997, is designed to determine release curves for each pollutant, depending on pH values. Eight different pH values in the range 4-12 are required to have a full characterization according to the technical specification. Each sample is suspended in water (ratio 1/10) and the pH is stabilized at the fixed value for 48 hours.
To guarantee a constant pH it is useful an automatic apparatus which set the pH at the desired valued for 48 h, adding the right amount of acid, or base, whenever it is needed. In our laboratory has been built up an automatic apparatus which can perform 4 tests simultaneously. pH is acquired by 4 glass electrodes and the signals, amplified by 4 specific electronic cards, are read by a DAQ connected by USB to a PC, which controls a 6-way electrovalve by RS232 protocol. The valve is fed by a peristaltic pump and provides to add the right amount of titrant to the each leaching vessels. In the first part, up to 4 hours, the system brings each vessel at the set pH value, and then checks if the test conditions are consistent with the method requirement (volume of added titrant and pH variation rate) or if the test must be aborted. Then the system corrects the pH deviations, due to liquid-solid equilibrium of buffer species, until the end of the test. The software is developed in LabVIEW environment. It allows to establish an easy communication between PC and instruments acquiring and generating signals. The software is in charge of reading signals from electrodes, elaborate them according with data provided by users, and controls the valve moving in order to correct the pH in the vessels when necessary. The output files are provided, with every data of the test management. The system is stable and able to manage 4 batches simultaneously, with none operator actions required, and provides the continuous control of the test during the whole 48 hours.
That tool has been tested to characterize contaminated sediments.

P87 - MONITORING OF H_2S REMOVAL BY GREEN SULFUR BACTERIA IN A BIOREACTOR USING GC-FPD

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Hydrogen sulfide is a poisonous gas that poses both environmental and industrial process concerns. It is present in many industrial effluents and is dangerous because it is toxic to humans, corrosive and poisonous to many catalysts. It is also present in biogas and must be removed because it poses a threat to engines and pipelines. In Italy, a limit of 5 ppm is imposed on biogas to be distributed in the national network. Processes for the removal of hydrogen sulfide from industrial effluents have been proposed [1] and analytical methods for their monitoring implemented [2].
In the UTRINN-BIO laboratory in ENEA a process for the biological removal of H_2S from biogas is currently investigated. Biogas is bubbled in a reactor containing green sulfur bacteria. Bacteria then oxidize sulfide to elemental sulfur and the biogas is ideally free to leave the reactor cleaned of hydrogen sulfide. For the monitoring of efficiency of bacterial oxidation, a method based on gas chromatography-FPD detection is here proposed. Briefly, a known amount (20 μL) of reactor medium is sampled in a closed vial and an excess of sulfamic acid is added. The headspace is then sampled and injected in the GC. Calibration is linear using sodium sulfide solutions as standards in the range 1-10 μM, limits of detection 0,5 μM.
The results from these analyses complement ones from the monitoring of exiting biogas and give information on the trend of bacterial oxidation in the reactor. It is also a safe method because there is no need to calibrate the system using H_2S- an operation that would pose a potential threat to the operator and an additional burden in safety requirements and costs. Also, it is simpler and safer than colorimetric method based on the formation of methylene blue [3]. Finally due to its simplicity it is fit for automation both in sampling and analytical part, an important element for a protocol that can be potentially used in the monitoring of a continuous process.

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P88 - DETERMINATION OF Os(VIII), Ru(III) AND Pb(II) IN VEGETABLE MATRICES, POTENTIAL BIO_MONITORS, BY SQUARE WAVE CATALYTIC ADSORPTIVE VOLTAMMETRY (SWCAdV)

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The introduction and increasing use of catalytic converters, containing platinum group metals (PGMs), are the cause, in the environment, of a higher concentration of these metals and a consequent and simultaneous decrease of Pb(II) concentration. This is the direct consequence of a growing and general distribution of fine particulate matter originating from damage or abrasion of the catalysts themselves.
In fact, after the first massive use of platinum, palladium and rhodium in the construction of catalytic converters, there was a gradual reduction of these PGMs and a growing use of osmium and ruthenium, because of their extreme hardness and resistance to very high temperatures .
This paper proposes a method for the simultaneous voltammetric (Square Wave Catalytic Adsorptive Voltammetry, SWCAdV) determination of Os (VIII) and Ru(III) in the presence, but also in the absence of Pb(II) −these metals are always simultaneously present in airborne particulate matter −in vegetable matrices. This choice is due to the fact that, in perspective, the vegetable matrices can be used as bio-monitors for environmental pollution by metals associated with vehicular emissions. The analytical procedure was verified through the analysis of standard reference materials: BCR-CRM 062 Olive Leaves and Tomato Leaves NIST-SRM 1573a. Precision and accuracy, expressed respectively as relative standard deviation and relative error, were generally lower than 6% in all cases, while the limits of detection for each element were lower than 5.0 $\mu g\ kg^{-1}$.
Once set up on standard reference materials, the analytical procedure was transferred and applied to laurel leaves sampled in proximity of a heavily trafficked road and of a remote zone considered non-polluted (Po River mouth area).
A critical comparison with spectroscopic measurements is also discussed.

P89 - CHARACTERIZATION OF THE ELEMENT CONTENT IN LACUSTRINE ECOSYSTEMS IN TERRA NOVA BAY, ANTARCTICA

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In this work nine lacustrine ecosystems belonging to four areas of Terra Nova Bay, Northern Victoria Land, Antarctica, were investigated in order to gain insight into the natural processes regulating species distribution and to point out the occurrence of possible present or future local and/or global anthropogenic contamination [1]. Major, minor and trace elements were determined in freshwater, algae, mosses and (for one site) lichens. Lake water composition was found to be influenced by several factors: marine spray, weathering of rocks and sediments, input of meltwater, presence of biological activity and lake geographical position. Algae show generally higher concentrations of elements than mosses and the calculated enrichment factors confirmed the capability of algae to bio-accumulate elements from waters, not only nutrients but also potentially toxic metals. Data were treated with chemometric techniques; principal component analysis showed interesting correlations among elements, which were interpreted taking into account their sources and chemical behaviour [2]. Hierarchical cluster analysis highlighted differences and similarities among the investigated lakes. No evidence of anthropogenic contamination was found, so it can be assumed that element distribution in such ecosystems still represents the result of natural processes.

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P90 - DETERMINATION OF EMERGING POLLUTANTS AND ENDOCRINE DISRUPTERS IN DRINKING WATER BY LIQUID CHROMATOGRAPHY - TANDEM MASS SPECTROMETRY

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Access to drinking water is important for human health, for the purposes of nutrition, personal hygiene and cleanliness, and is a social and political right required for development opportunities. Among the various compounds of anthropogenic origin that are found in raw water for human consumption (e.g.: pesticides, heavy metals, solvents etc.), the scientific community has identified a new class of pollutants, namely Endocrine Disruptors (EDs) [1].
EDs are a group of chemicals, of natural and synthetic origin, which are present in the environment and are suspected to alter the function of the endocrine system and consequently cause adverse effects on organisms. The identification of these compounds requires the use of advanced scientific instrumentation and a support by specialized structures.
In the framework of a collaborative project [2], a liquid chromatography-electrospray ionization-tandem mass spectrometry method was developed for the determination of emerging pollutants (e.g. estrogens and pharmaceuticals), using two different mass spectrometry techniques (triple quadrupole and ion trap) [3].
Quantitative analysis was performed in multiple reaction monitoring (MRM) using internal standards (perdeuterated compounds, when possible).
The method was applied to the determination of the analytes in different samples of water intended for human consumption; recently obtained results will be presented here.

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P91 - QUANTITATIVE RELATIONSHIP BETWEEN CHARGE STATE OF SODIUM DOCUSATE (AOTNA) CLUSTERS AND CONE VOLTAGE.

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Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) is characterized by the presence of two hydrophobic chains that, in apolar solution, guarantee the reverse micelle formation (Figure1).
Considering the several applications of this molecule in technological and industrial fields, it seemed of interest to study the gas-phase properties of surfactant molecules [1,2]
Using Electrospray Ionization (ESI)-Mass Spectrometry investigations, we observed the formation of positively charged large clusters as $[(NaAOT)_n+Na]^+$ or negatively clusters as $[(NaAOT)_n-Na]^-$ with n up to 22.
The ESI/MS spectra of $AOTNa^+$ aggregates showed exclusively singly charged species at high cone voltage values, but at lower cone voltage values the MS spectra the double charged species became predominant.
Plotting the abundance ratio of doubly charged versus singly charged ion intensities at the same cone voltage values and at the same equal aggregation numbers, the shape of the curve can be described by the equation:

$$Y= Ax^2+Bx+C$$

The graph shows an exceptional regularity of the abundance ratio of doubly charged versus monocharged ion intensities on the same aggregation number.
The doubly charged fragmentation pattern has been investigated using a Q-ToF instrument for MS/MS analyses of positively charged aggregates.
The MS/MS experiments show that at lower aggregation numbers (n from 2 to 6) singly charged species are the only obtained but, at higher aggregation numbers, also the formation of doubly charged fragments, due to neutral species loss, takes place.

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P92 - TANDEM MASS SPECTROMETRY WITH DATA DEPENDENT ACQUISITION FOR THE DETERMINATION OF UV FILTERS IN URBAN WASTEWATER TREATMENT PLANTS

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Organic UV filters, molecules with the capability to absorb UV radiation, are widely used in personal care products (skin creams, hair sprays, body lotions, hair dyes etc.) and in industrial goods such as paints, plastics, or textiles. These chemicals have recently been included in the list of emerging contaminants [1] due to their increased use and occurrence in environmental waters and because of their potential adverse health and environmental effects. Preliminary studies on animals indicated that some organic UV filters have considerable endocrine disrupting effects [2]. Generally, methods for the analysis of UV filters are based on chromatography and related techniques, electroanalysis, spectroscopy and mass spectrometry [3]. Several sample pre-treatment methods are commonly used to selectively extract UV filters at ultra-low concentration levels. In our laboratories a method using stir bar sorptive extraction (SBSE) followed by LC-MS/MS was developed and subsequently optimized for the determination of UV filters in different water matrices [4, 5].
In this work, the occurrence of six of the most commonly used UV filters with endocrine-disrupting potential was investigated in the influent and the effluent in different Wastewater Treatment Plants (WWTPs) of Genoa - Italy. The analytes were extracted by SBSE and analyzed by LC-MS/MS. Quantitative analysis was performed in triggered MRM, a data dependent acquisition of the signal, which allowed to obtain both sensitivity and specificity. In the inlet samples four analytes were detected in the range 4-163, 12-390, 23-68, 2-4 ng/L, respectively; higher inputs of UV filter to WWTPs during the warmer months were highlighted.

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P93 - ULTRATHIN Si NANOWIRES AS PROMISING SUBSTRATES FOR SURFACE-ASSISTED LASER DESORPTION IONIZATION MASS SPECTROMETRY

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Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) represents an invaluable technique for the analysis of high molecular weight analytes. However, some drawbacks, such as spectral interferences and limited reproducibility, have been correlated to the use of conventional MALDI organic matrices for the analysis of low-molecular weight (LMW) compounds. Nanomaterials are being frequently proposed to overcome these problems, and sub-techniques like surface assisted or enhanced LDI-MS (SALDI-, or SELDI- MS) are rising an increased attention. Au- and Si-based nanomaterials have been frequently demonstrated to outperform conventional matrices in specific LDI-MS applications and the literature on this subject has been recently reviewed in several papers [1, 2].
In the present study, Si nanowires (Si NWs), prepared in the CNR laboratories by a maskless wet-etching technique, assisted by the deposition of an ultrathin gold film on a Si substrate [3], are proposed as DI promoters for SALDI-MS.
SALDI-MS characterizations have been carried out on different LMW analytes, such as amino acids, peptides, lipids, etc.. Different NW lengths have been used, in the range comprised between 100 and 1000 nm and the relevant data have been combined with surface spectroscopy and morphological characterizations, in order to correlate the nanomaterial properties and MS performances. Si NWs provide interesting LDI-MS spectra with very limited interfering peaks, if any. The feasibility of the use of Si NWs in SALDI-MS platforms has been proved.

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P94 - A STRATEGY FOR THE INTEGRATION OF RECOGNITION ELEMENTS IN EGOFET BASED BIOCHEMICAL SENSORS

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Organic Field-Effect Transistors (OFETs) have been widely studied as small, disposable and cheap devices for biochemical sensing [1]. In the present work an OFET biosensor selective for the C-reactive protein (CRP) was developed. Here, besides to provide an innovative strategy to integrate bio-recognition element in an electronic device, the selectivity of the OFET based biosensors towards a target bio-analyte was also tested. The selectivity was reached by using an anti-CRP antibody layer able to specifically capture the CRP. To immobilize the anti-CRP on the poly(3-hexylthiophene) (P3HT) organic semiconductor (OSC), the OSC surface was first covered with an hydrophilic polymeric coatings, characterized by –COOH groups, using plasma enhanced vapour chemical deposition (PE-CVD). Such process allow the deposition of a few nanometers-thick-coating rich in —COOH groups which has already been proven to minimally affect the OFET electrical performances [2] and can be effectively used to immobilize bio-receptors onto the Electrolyte-Gated OFETs device [3]. The functional groups were in fact used as anchor sites to covalently attach a biotinylated phospholipids layer on the OSC. The biotinylated phospholipids furnish the binding sites for streptavidin or avidin proteins that are then used to immobilize the biotinylated anti-CRP antibody. The response of EGOFET devices embedding an anti-CRP layer was compared with that of devices without the anti-CRP layer. All the transistors were tested using PBS 10 mM as gate dielectric before and after the incubation of the CRP. The results indicate a good selectivity of the transistor towards the CRP.

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P95 - ANALYTICAL PERSPECTIVES OF TAURINE/GRAPHITE OXIDE ELECTRODE COATINGS

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Surface modifications of electrodes aimed at confering them appealing features, such as increased sensitivity and selectivity, still receive a continuously growing attention. Amongst the possible modifiers, are worth mentioning sulphonated species, such as Nafion, poly(p-aminobenzene sulfonic acid), cysteic acid, poly(p-toluene sulfonic acid) and so on [1]. All these species (except Nafion, that is directly casted onto the electrode) are deposited by electrochemical oxidation, either potentiostatically or by cyclic the potential in a wide range.
The applications of these sensors are quite widespread [1], spanning from inorganic ions to drugs, pharmaceuticals, herbicides, pollutants, biological fluids, etc.
In this contribution, a new type of modified electrode, based on the deposition of a taurine/graphite oxide film onto glassy carbon (GC) electrodes is proposed. The modification of the electrode is achieved by potentiostatic oxidation in a taurine solution using pH 7 phosphate buffer as supporting electrolyte.
The modified electrode presents attractive features, such as permselectivity against anions and preconcentration of cations, leading to substancially increased selectivity and sensibility with respect to bare GC electrodes.
The research is in progress, especially for evaluating possible applications to the analysis of species of alimentary concern in real samples. In fact, the permselectivity of the modifying layer should be particularly effective in avoid fouling and adsorption phenomena frequently seen in real matrices.

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P96 - COMPARING REGRESSION RELATIONSHIPS: APPLICATION TO CHEMICALLY MODIFIED ELECTRODES.

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When developing new chemically modified electrodes (CMEs), as currently done in this laboratory, attention is always paid to carefully evaluate their experimental performances [1-3]. This is especially needed after some tentative modifications of experimental conditions. Comparing regression relationships (RRs), usually obtained by ordinary least square regression, may help in deciding the right direction towards the optimization of electrode performances. This implies evaluating if significant differences exist between slopes and/or intercepts of RRs, hence if experimental differences arise only by inevitable random errors or not. In practice, the necessary tests should allow verifying if the considered regression relationships come from the same RRs population from which the actual samples are drawn. It was suggested that such a kind of comparisons can be performed by specific Student's t-tests [4]. The flow chart for comparing two RRs is presented in the figure.

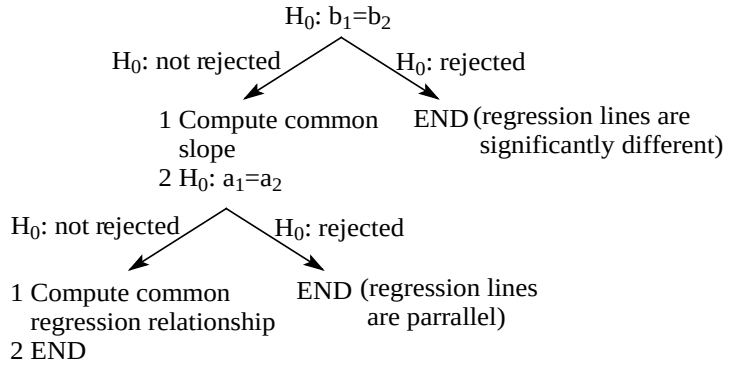

Figure: Flow chart for the regression of two RRs; b: slopes; a: intercepts.

Comparing more that two RRs is also possible by similar tests [4]. The matter is presented with the help of specifically developed Mathcad worksheets. Some examples are described by using simulated results as well as results relevant to CMEs developed in this laboratory.

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P97 - MICROSTRUCTURING CONDUCTING POLYMERS AND MOLECULARLY IMPRINTED POLYMERS BY LIGHT-ACTIVATED ELECTROPOLYMERIZATION ON MICROMACHINED SILICON. APPLICATIONS IN ELECTROCHEMICAL SENSING.

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A novel trend in the conducting polymers (CPs) field is oriented towards the design of micro/nanostructured CPs [1] motivated by their unique features with respect to those of bulk materials, such as enhanced conductivity and higher mass transport rate. Particularly in CPs sensing applications [2], the effect of micro/nanosizing revealed to determine shorter response time and higher sensitivity. Such a trend is in fact observed also in the field of CPs-based Molecularly Imprinted Polymers (MIPs) [3], tailor made synthetic receptors with molecular recognition properties. Although different approaches have been proposed for micro/nanostructuring CPs and CPs-based MIPs, limited morphological features have been achieved so far. Higher flexibility in CPs microstructuring can be obtained by the novel proposed technology combining CP electrosynthesis with electrochemical silicon microstructuring, the latter allowing the fabrication of 3-D silicon structures with sub-micrometer accuracy. Light-activated electropolymerization on micromachined *n*-type silicon (*n*-Si) is here proposed as a versatile root for microstructuring CPs and MIPs. Several CPs (polypyrrole (PPy), poly-3,4-ethylendioxythiophene, poly-3-methylthiophene, polythiophene) and a PPy-based MIP are successfully grown on microstructured *n*-Si templates. Each polymer shows highly conformal replication of the template features for all microstructures independently of aspect-ratio values, as revealed by Scanning Electron Microscopy (SEM) analysis. Microstructured CPs chemical structure and conductivity are studied by spectroscopic and electrochemical analyses, respectively, the latter showing the increase of the electroactive area due to microstructuring. Experimental conditions for the light-activated electropolymerization of a PPy-based microstructured MIP for SDM have been optimized. Its performance in the electrochemical detection of SDM reveals a good imprinting effect, evaluated by MIP and NIP (not-imprinted polymer) amperometric responses to SDM in a flow system. Also the current response increase on microstructured MIP with respect to the flat one is verified.

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P98 - AMINE OXIDASES BASED BIOSENSORS FOR BIOGENIC POLYAMINES DETERMINATION

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Amine oxidases are ubiquitous soluble enzymes which catalyze the oxidative deamination of the amines to the corresponding aldehydes, ammonia and hydrogen peroxide; the generic reaction is as follows:

$$R\text{-}CH_2\text{-}NH_2 + O_2 + H_2O \rightarrow R\text{-}CHO + H_2O_2 + NH_3 \qquad (1)$$

These enzymes have been found in various microorganisms, plants and animals [1].
The chosen amine oxidases were either polyamine oxidase (PAO) that has a substrate specificity for natural polyamines (as spermidine (Spd) and spermine (Spm)) and spermine oxidase (SMO) that oxidizes only the latter substrate. Measurements of the oxygen consumption or the hydrogen peroxide production are commonly used for assaying the enzyme activity.
This work describes the assembly and optimization of electrochemical biosensors for specific determination of biogenic polyamines reported above. Electrochemical biosensors have been prepared using polyamine oxidases entrapped in poly(vinyl alcohol) bearing styrylpyridinium groups (PVA-SbQ), a photo-cross-linkable gel, onto electrode surface.
The obtained sensors are sensitive to the addition of various biogenic and synthetic polyamines, whose determination may be of importance either in research and in food analysis and in the diagnostics of certain diseases [2].
Biosensor performances were evaluated in flow injection amperometric systems (FIA) and the modified electrodes showed a good sensitivity, long term stability and reproducibility. The kinetic parameters, the apparent Michaelis constant (K_M) and the steady-state current (I_{max}) were determined by the classic Michaelis-Menten equation [3].
The proposed method was also successfully applied in the determination of biogenic amines in biological real samples with encouraging results.

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P99 - DNA-BIOSENSOR FOR Hg^{2+} DETERMINATION BASED ON POLYTHYMINE-METHYLENE BLUE MODIFIED GOLD SURFACE AND ELECTROCHEMICAL TRANSDUCTION

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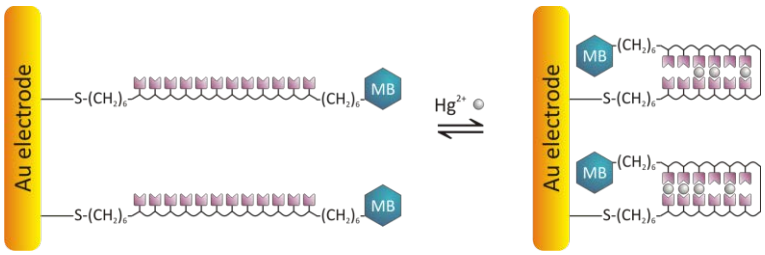
Mercury is one of the most worrisome environmental contaminant; among its various forms, the EPA (Environmental Protection Agency) has set the limit at 10 nmol L^{-1} concentration of mercury (II) in drinking water [1].
In recent years, it was demonstrated that the determination of Hg^{2+}can be employed with an excellent degree of selectivity by the use of DNA biosensors through the formation of the complex Thymine-Hg-Thymine (T-Hg-T): in fact, Hg^{2+} tends to bind two thymines, generating a T-Hg-T complex with a formation constant higher than that one of the coupling Adenine-Thymine,which can be employedfor a selective, fast and cost-effective Hg^{2+} detection[2,3].



In this work we have developed a new electrochemical DNA biosensor for the selective determination of the ion $Hg^{2+}$by the use of a gold electrode where polythymine modified in 3' position with Methylene Blue as redox probe, was immobilized. The presence of the Hg^{2+} in solution leads to formation of the complex T-Hg-T thus causing the "hairpin-like" folding of oligonucleotide, leading to an improved electronic exchange of methylene blue with the gold electrode and thus to an increase of the faradic current which is detected by means of square wave voltammetry (SWV).
The biosensor displayed to be sensitive to Hg^{2+}concentration in the range 5-2000 nmol L^{-1} with a LOD of 2 nmol L^{-1}.

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P100 - DEVELOPMENT OF ELECTROCHEMICAL AFFINITY BIOSENSORS FOR THE DETECTION OF TUMOR NECROSIS FACTOR ALPHA USING DIFFERENT LIGANDS

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TNF-α is an inflammatory cytokine produced by the immune system. Serum TNF- α level is elevated in some pathological state such as septic shock, graft rejection, HIV infection, severe meningococcemia, neonatal listeriosis and rheumatoid arthritis. Detecting trace amount of TNF-a is very important for the understanding of tumor biological processes. Analysis of this key biomarker is commonly achieved by use of an ELISA.
In this study, we show that, by replacing the traditional colorimetric detection with differential pulse voltammetry (DPV) and the traditional plastic wells with a screen-printed array of electrodes, simultaneous electrochemical analysis of different samples can be achieved.
A commercial human TNF-α matched antibody pairs were used to achieve the analysis of TNF-alpha. Moreover, twootheraffinitymolecules, produced by evolutionaryapproaches, namely a nucleic acid aptamer and a combinatorial non-immunoglobulinprotein,known to interact with TNF-α selectively, have been tested as detection ligands.
These molecules were tested in different assay format both using gold electrodes or magnetic beads as support for bioreceptor immobilization.
Preliminary results of serum samples analysis were also reported.

P101 - COMPARISON OF TWO DIFFERENT AMPEROMETRIC ENZYME SENSORS FOR ETHANOL DETERMINATION IN ALCOHOLIC BEVERAGES

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Two different enzyme electrodes for the determination of ethanol in alcoholic beverages were developed by immobilizing alcohol oxidase or catalase in a k-Carrageenan gel layer overlapping an amperometric gaseous diffusion Clark type oxygen electrode. The variation of the oxygen concentration in the aqueous solution due to the enzymatic reactions was measured at a constant potential of – 650 mV. Biosensor response to standard solutions of methanol, ethanol, n-propanol, n-butanol, ethylenglycol and glycerol was recorded, compared and discussed. All the experiments were carried out at 23°C in a thermostated reaction cell containing 15 mL of 0.05M phosphate buffer solution. The effect of pH on the response of the electrodes was investigated in detail and the best pH was found to be 7.5 for the catalase electrode and 8.0 for the alcohol oxidase electrode, respectively. In the biosensor characterization studies several parameters such as operational stability, response time, analysis time, measurement and calibration repeatability, inter-day and inter-electrode calibration reproducibility, linearity, sensitivity and substrate specificity were recorded. The response of the catalase biosensor was not influenced by the presence of the methanol and the stability of the catalase layer was about three times longer than that of the alcohol oxidase. Finally, the ethanol concentrations of several wine and beer samples were determined using the biosensors developed and the results obtained with the two enzyme electrodes were compared. The precision and accuracy of the two methods were similar and the recoveries were greater than 90% for both biosensors. The biosensor method using catalase enzyme seemed to be the more selective and less expensive of the two enzyme devices for the determination of ethanol in alcoholic beverages. The catalase enzyme electrode showed greater selectivity to ethanol out of all the alcohols tested, and its operational stability was significantly higher than that of the alcohol oxidase sensor. The only drawback associated with the use of the catalase biosensor, compared to the method based on alcohol oxidase, is the slightly longer time required to perform the ethanol analysis in each alcoholic beverage sample. This limit is significant only if a series of analyses of several samples must be carried out in succession.

P102 - ELECTROSYNTHESIS OF ZINC OXIDE NANOPARTICLES AS PROMISING MATERIAL FOR SENSING APPLICATIONS

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The development of low cost devices for biosensing applications is a hot topic in both academic and industrial research. Nanomaterials may offer excellent prospectsfor designing a new generation of bioelectronic devices. In particular, the high surface area exhibited by nanostructuresoften results in an amplification of the biosensor response [1]. Among the wide variety of inorganic nanomaterials, zinc oxide nanoparticles (ZnO-NPs) are appealing because of their biocompatibility, high surface area,and excellent electron transfer and semi-conducting properties. Furthermore,ZnO-NPs may be easily functionalized and show generally good binding ability for biomolecules [1]. In this communication, we report on the electrochemical preparation of ZnO-NPs in aqueous solution at constant current [2] in the presence of different surfactants, and at different temperatures. Calcination of electrosynthesizednanocolloids was also carried out at 300 °C and 600 °C to improve the ZnO content.Sodium polystyrene sulfonate (PSS),which is frequently used as stabilizer for nanoparticles in biosensing applications, was selected as dispersing agent due to its biocompatibility. Moreover, the negative charge carried by PSS may also promote the interaction with both ZnO-NPs and biomelecules[3]. ZnO-NPs were morphologically characterized by TEM microscopy,and chemically analyzed by UV-Vis, IR and XPS spectroscopies.
Preliminary experiments on the use ofZnO-NPs in combination with a bioelectronicOFET [4]to evaluate potential signal amplification effect [5]will be also shown.

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P103 - COMMERCIALLY AVAILABLE EDIBLE JELLY AS A NOVEL DIELECTRIC FOR ORGANIC THIN FILM TRANSISTORS.

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Organic thin film transistors are gaining importance in biosensors development because of low cost and ease of fabrication [1]. Possibility of fabricating OTFTs on flexible substrates using well established mass fabrication methods is an added advantage for organic transistors over its inorganic counterparts [2]. Development in all organic transistors with polymer dielectrics in place of inorganic Si/SiO_2 dielectrics has opened new doors of integrating bio-recognition elements directly into the dielectric material. Recently, electrolyte gated organic thin film transistors were demonstrated employing water or PBS as dielectric [3]. This has opened new era of liquid gated transistors which can be beneficial in the development of biosensors used for label free detection in liquid media. Fast evaporation of water makes bio-sensing difficult when water is used as dielectric. To overcome this drawback hydrogels based on organic polymers such as PVA, PAA, PMMA can be used as dielectric. Hydrogel enables lateral transport of ionic species and reduces evaporation rate of liquids contained within its matrix.

Nature is our best teacher. We present novel dielectrics by employing commercially available edible polyelectrolyte jelly in electrolyte gated OTFT on flexible substrate. Organic thin film transistors in bottom contact top-gate and bottom contact lateral gate configurations were investigated employing jelly as a dielectric. Polyelectrolyte jelly enhances the electrical figure of merits at least by one order of magnitude. Such a dielectric material can be used for the development of biosensors employed in food quality control.

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P104 - DETECTION OF SPECIFIC IgE TO G5 AND D2 AEROALLERGENS THROUGH AN ELIME ASSAY

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Allergic diseases, known as "hypersensibility diseases", are chronic inflammatory conditions caused by exposure to a variety of external agents called *allergens* [1]. Immunoglobulin E (IgE) is a key mediator of type 1 (atopic) allergic disease provoking asthma, allergic rhinitis and atopic dermatitis [2,3] and its dosage is currently necessary in the clinical practice of allergies diagnosis. A new, rapid magneto-electrochemical immunoassay for allergy's diagnosis has been developed and applied to human serum samples analysis. The ELIME (Enzyme-linked ImmunoMagnetic Electrode) system [4-5] uses Dynabeads® Tosylactivated magnetic beads coated with a monoclonal antibody able to bind human IgE. It was used a secondary monoclonal antibody anti-hIgE or target allergens, both conjugated with biotin, to analyze generic IgE standard solutions and specific IgE in serum samples, respectively. The biotin bonds streptavidin conjugated with alkaline phosphatase (AP). Differential pulse voltammetry (DPV) measurements, using an array of 8 magnetized screen-printed electrodes coupled with a portable potenziostat instrument, are carried out after the addition of α-naphtyl phosphate, which is enzymatically converted into the electroactive naphtol product. We focused our attention on two common aeroallergens as G5 (*Lolium perenne* from Graminacea family) and D2 (*Dermatophagoides farinae*, dust mite) optimizing several assay parameters such as the MAb/allergens-biotin diluitions and the streptavidin–AP concentration. Subsequently, we analyzed 38 serum samples, whose specific IgE levels were independently determined by our University Hospital (PTV), using routine kits. We correctly classified all the sera, except for one sample, in accordance to PTV results. LOD and LOQ of the electrochemical assay, determined by 20 measurements of a blank serum sample (negative for G5 and D2), resulted to be 0.10 and 0.15 KIU/L, respectively. Analysis of other serum samples are in progress to make a ROC curve and establish the clinical sensitivity and specificity, and cut-off value of our method.

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P105 - REPORTING ANALYTICAL PERFORMANCES OF ELECTROCHEMICAL SENSORS. SOME SUGGESTIONS.

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A careful description of the performances of electrochemical sensors is of critical importance for evaluating their novelty and potential applications. This usually requires the evaluation of some figures of merit, such as linear range (and the relevant functional relationship), limits of detection and quantification, recovery, trueness, selectivity and precision. Of course, testing a new electrochemical sensor does seldom need a complete validation study. This should be only necessary when developing an analytical method based on the use of that sensor. Most frequently, papers are mainly aimed at reporting details of the method used to prepare the sensor and of the experiments used for characterizing its chemical/electrochemical/morphological features. But, if some analytical performances of the proposed sensor are evaluated, than the reported figures of merit should allow a reasonably appropriate interpretation. However, while reviewing a series of paper dealing with some chemically modified glassy carbon electrodes [1], it was noticed that quite often the figures of merit presented to the readers were ill-defined and/or reported in an inadequate/wrong format [1,2].
In such a situation, some simple suggestions about how the above mentioned electrode performances should be reported might be quite useful. Based on many well-known books and guidelines, this contribution is aimed at suggesting how incorrect/unreasonable statements can be avoided when describing the analytical performances of a given sensor. The matter is presented with the help of few examples inherent to chemically modified electrodes.
Authors wishing to report reasonably correct, unambiguous and clearly interpretable descriptions of the performances of their sensors will certainly front a certain (but not necessarily unsustainable) increase of costs and times of their investigations, but the results should gain an easier acceptance and applicability by the scientific community.

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P106 - ELECTROANALYSIS OF NITRATE WITH ENSEMBLES OF COPPER NANOWIRE ELECTRODES

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Nitrate is assessed in different contexts like ecosystems, physiological processes, food production, and others. Typical examples are the maximum permissible concentrations of nitrate in drinking water (<45 mg L^{-1} - < 0.73 mM for adults and < 10 mg L^{-1} - < 0.16 mM for infants), and the monitoring of nitrate concentrations in the production and processing of foods. The requirement of developing sensitive analytical tools for the monitoring of nitrates is evidenced by the fact that nitrate can be involved as precursor in the formation of endogenous N-nitrous compounds (nitrosamines and nitrosamides) with carcinogenic activity as well as, in causing the "blue-baby" syndrome or methemoglobinemia [1]. In terms of electroanalytical determination of nitrate, various strategies have been proposed based on the use of reactive metal substrates, boron doped diamond electrodes, surface or solution based catalysts, or suitable biocatalysts [2-4]. The use of bare copper electrodes for direct nitrate analysis could be the most attractive option, however it presents important problems such as low sensitivity and reproducibility [2]. In the attempt to improve the analytical performances of copper electrodes, we report the results of a study aimed at optimizing the electrochemical reduction of nitrate at ensemble of copper nanowire electrodes (CuNWEs). The nanowire electrodes were obtained in our laboratory by template electrochemical deposition of Cu in the pores of track-etched polycarbonate (PC) membranes (400 nm in diameter), followed by dissolution with CH_2Cl_2 of the PC. The electroanalytical performances of CuNWEs for nitrate analyses were assessed and compared with those of Cu-flat electrodes as well as, of different kinds of nanostructured Cu electrodes recently proposed in the literature [2, 3].

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P107 - TOWARDS FORENSIC ANALYSIS: ADSORBITIVE STRIPPING DETERMINATION OF LSD

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LSD is one of the best known and most active hallucinogens. Known determination methods of LSD and its congeners derived from lysergic acids are based on HPLC coupled with fluorescence detection[1]; due to ergots alkaloids electrochemical properties [2] in this study we propose an electroanalytical method based on the oxidative adsorptive stripping voltammetric of LSD accumulated at a glassy carbon electrode The method operates in a non-aqueous electrolyte based on a solution of tetrabutylammonium perchlorate in DMF, although up to 10% water can be easily tolerated. The accumulation step is performed at a -300 mV applied potential, and the stripping step give rise to a peak centered at +1100mV.
The influence of the electrochemical parameters was deeply investigated, and the electrochemical process was characterized by cyclic voltammetry.
The method is very sensitive and allows determination of the drug at ppt levels with only 60 s deposition time
Recovery from biological samples spiked with feasible amounts of the drug was tested with good results. In particular, recovery from urine, hair samples and stamps impregnated with LSD was attempted. The influence of possible interference (caffeine, mescaline, amphetamine) was explored as well.

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P108 - TBSENSE - POINT OF CARE DEVICE FOR TUBERCULOSIS DETECTION

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Despite the fact that tuberculosis (TB) is a curable disease it remains a major global problem. TB is a significant public health threat and economic burden, particularly in developing countries. The combination of inadequate treatment and sometimes the complexity of medical practices exponentially increases the morbidity and mortality rates of tuberculosis patients. The task of arriving at an accurate medical diagnosis may sometimes become very complex and difficult.

The aim of this work is the development of a point-of-care detection system for the detection of TB. This device is further able to discriminate latent tuberculosis from its active form.

The system, based on electrochemical detection techniques, will be evaluated for the measurements in saliva, where concentrations of biomarkers and antibodies are expected to be low. Four points are in focus for these sensors: simplicity of use, robustness, low-cost fabrication and suitability for mass production.

In this work the possibility of using screen-printed electrodes (SPEs), as the support for sandwich-type immunoassay is evaluated. For a first proof of concept, a sensor for the detection of alpha-amylase in saliva has been developed. Due to the abundance of alpha-amylase in saliva (40 to 50% of the total protein content of human saliva), this marker has been chosen as the positive control for the test.

Alpha-amylase detection is performed by a sandwich immunoassay, either directly immobilized on the SPE surface or on the surface of magnetic beads. The secondary antibody is conjugated with HRP and the successful formation of the sandwich is then detected by chronoamperometry, after addition on the surface of SPE of a few microliters of a mixture consisting of hydroquinone + H_2O_2. The use of magnetic beads could potentially enhance the current signal, concentrating multiple HRP molecules on the sensor surface, and function as a pre-concentration system, making possible the treatment of a larger volume of saliva.

Experiments to evaluate the matrix effect on real saliva samples are in progress. The next step will be to adapt the system to the detection of tuberculosis using the biomarker ESAT-6.

P109 - SENSITIVE AND INTERFERENCE-FREE GLUTAMATE AMPEROMETRIC BIOSENSOR FOR THE MONITORING OF FOODSTUFFS

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L-Glutamate (Glu) is a well-known flavour enhancer that is present in several foodstuffs either as an additive or a natural compound. Glu monitoring is an important issue since the excessive intake of this flavour enhancer can cause allergic and neurotoxic effects. Glu is currently determined by chromatographic [1] or capillary electrophoretic [2] methods, which require extensive sample pre-treatment and expensive equipments. A suitable alternative is represented by amperometric biosensors, low cost devices that could provide specific, rapid and repetitive analyses of complex matrices. In the last decade a number of biosensors for glutamate detection have been proposed [3-7], but the above mentioned requirements have not been completely met. In order to face these problems a proper selection of the electrode material and the use of permselective films are required [8].
This work describes the development and optimization of an amperometric biosensor for glutamate monitoring in foodstuffs. The biosensor is based on glutamate oxidase (GLOD) immobilized by a gel of bovine serum albumine and glutharaldeyde onto a platinum electrode modified with a permselective overoxidized polypyrrole film. Different experimental conditions have been tested for the enzyme immobilization, and the optimized biosensor, integrated in a flow injection system, has been characterized in terms of linearity, LOD, LOQ, repeatability and stability of response. The excellent anti-interference characteristics towards the main interferents present in real food matrices have allowed the application of the biosensor in the accurate monitoring of Glu in different kind of foodstuffs.

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P110 - ELECTROCHEMICAL IMPEDANCE CHARACTERIZATION AND FT-IR ANALYSES OF ANTICORROSION SILICONEPOXY HYBRID SYSTEM COATINGS.

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The metallic structural equipments are prone to be attacked by aggressive species such as water, oxygen, and ions in natural environment.
The barrier properties of coatings play an important role on the protection against the corrosion of metals. [1],[2]
Thought the last, both organic and inorganic coatings have been widely applied for the protection of metals against corrosion.
Industry always seeks Eco compatible solution in this filed; in this contest Fraunhofer IFAM is actively developing coatings having high erosion resistance excellent tribological and anticorrosion properties.
In this study we have characterized by means of Electrochemical Impedance spectroscopy (EIS) and Fourier Transformed Infrared Spectroscopy (FT-IR) three novel siliconepoxy ecocompatible coatings and the results were compared to commercial paint.
The samples in exams showed a very good anticorrosion properties (Ecorr and water intake) comparable to the available commercial paints. Further study will be performed in order to increase the performance of the primer in exam before patenting them.

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P111 - OXYGEN TRANSFER IN A GAS-LIQUID SYSTEM: KINETIC INFLUENCE OF WATER SALINITY.

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Oxygen gas is widely used as oxidant in a variety of industrial processes, such as hydrometallurgy, biochemical industry, organic syntheses, and wastewater treatment [1].However, the gas–liquid mass transfer of oxygen usually becomes a bottleneck of the whole process due to its sparing solubility in aqueous solutions. It is therefore a research subject to enhance oxygen mass transfer.This study is dedicated to an accurate evaluation of thermodynamic and kinetics aspects in the water oxygenation process. Oxygenation can be analyzed by means of kinetic study of oxygen dissolution from the oxygen mass transfer coefficient (K_La) andoxygen transfer rate (SOTR) [2]. A stirred, submerged aerated 4-liters system have been designed and the operational conditions has been optimized by studying the influence of hydraulic head, air flow and salinity of water using an optical oxygen sensor. Concerning the thermodynamic phase equilibria, experimental and modelling results are obtained from different binary systems (water/air) and ternary systems (water/air/salts). This information is necessary to predict the composition of the gas phase during the process and it is also important for an implementation in a process simulation. The oxygen mass transfer coefficients were firstly measured, monitoring in the time the oxygen concentration in various synthetic liquid phases containing either salts (NaCl, KCl, LiCl and MgCl). When compared to clean water, noticeable increase of K_La were observed; the variation of K_La and SOTR with the solution salinity was modelled and found dependent on the nature of cation in the salt added. For all cases, an increase of K_La with salinity increasing was observed. The present study clearly confirmed the importance to define the experimental conditions before to describe and to model appropriately the gas–liquid mass transfer phenomena.

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P112 - SPECTROSCOPIC CHARACTERIZATION OF CADMIUM AND COPPER MODIFIED SMECTITES FOR SOIL REMEDIATION

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The presence of heavy metals in the environment is a potential risk for the ecosystem due to their toxicity to plant, animals and human life. Lots of technologies and treatments have been developed to remove them from aqueous solutions, employing natural or synthetic sorbents. Among them, clay minerals have revealed interesting properties in soil remediation due to their natural occurrence, low toxicity, and low cost. Moreover, mechanochemical processes allow to activate chemical reactions by inducing different kinds of mechanical stress and without any other energy supply. In this study the effect of mechanochemical treatments on the ability of dioctahedral and trioctahedral smectites to "entrap" heavy metals is investigated. To this purpose a dioctahedral smectite "bentolite L" and a trioctahedral one "laponite RD" were ground with different distinct amounts of copper and cadmium chloride in dry conditions by means of zirconia planetary ball mill.
Experimental tests were performed modifying the milling time and metal/clay minerals mass ratio, whereas grinding energy and ball to powder ratio were kept constant. The efficiency of the mechanochemical process to promote the interaction between smectites and heavy metals was evaluated by means of different analytical techniques: the immobilization degree was evaluated by ICP/OES analyses and expressed by the leachable fraction of metal ions. While the investigation on the main adsorption sites of the heavy metals on the ground surfaces was tested by means of solid-state measurements through the combined use of X-ray Fluorescence Spectroscopy, Fourier Transform Infrared Spectroscopy, X-ray Diffraction, Nuclear Magnetic Resonance and X-ray Photoelectron Spectroscopy.


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