Università
degli Studi di Messina

Società Chimica Italiana

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

Giardini Naxos (Messina)

18-22 Settembre 2016

www.analitica2016.it

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PRESENTAZIONE

Il Congresso che la Divisione di Chimica Analitica della Società Chimica Italiana organizza annualmente vuole essere un punto d'incontro e di confronto per tutti coloro che svolgono la propria attività nella ricerca chimico analitica.
Il XXVI Congresso si svolge da domenica 18 a giovedì 22 Settembre 2016 a Giardini Naxos, presso l'AtaHotel Naxos beach e si articola in sessioni scientifiche volte a coprire i principali settori della Chimica Analitica.

I principali argomenti di discussione sono i seguenti:

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

L'organizzazione è curata dai gruppi di Chimica Analitica dell'Università degli Studi di Messina.

Programma

Domenica 18 Settembre 2016

17.00 – 21.00 Registrazione dei partecipanti (Atahotel Naxos Beach)

19.00 – 21.00 Cocktail di benvenuto

Lunedì 19 Settembre 2016

Dalle 8.30: Registrazione dei partecipanti (Atahotel Naxos Beach)

Sala "Naxos Alcantara"

9.00 – 9.30 Apertura del Congresso

9.30 – 10.15 Conferenza Plenaria **PL1 –** Chairman: ***Luigi Mondello***

Janusz Pawliszyn (University of Waterloo, Canada)

DEVELOPMENT OF ANALYTICAL DEVICES AND PROCEDURES CONSISTENT WITH GREEN CHEMISTRY

10.15 – 10.45 Conferenza Vincitore del Premio Giovane Ricercatore **GR1**

Marco Minella, C. Minero (Università di Torino)

DETERMINATION OF GASEOUS SPECIES TRANSFORMATION RATE IN FLOW REACTORS: SOME CASE STUDIES OF ENVIRONMENTAL CONCERN

10.45 – 11.00 Coffee Break

Sessione Parallela: **Ambiente 1 -** ***Sala "Naxos Alcantara"***

Chairman: ***Claudio Minero***

11.10 – 11.40 **KN1** *COMPOSITION, SOURCES AND MITIGATION STRATEGIES FOR PM10 AND PM2.5 IN SOUTH EUROPE. MAIN RESULTS FROM THE LIFE+ AIRUSE PROJECT.*

R. Udisti[1], M. Chiari[2], M. Giannoni[2,3], F. Lucarelli[3], S. Nava[2], G. Calzolai[3], S. Becagli[1], R. Traversi[1], X. Querol[4], F. Amato[4], V. Gianelle[5], C. Colombi[5], C. Alves[6], D. Custódio[6], K. Eleftheriadis[7], E. Diapouli[7], R. Harrison[8], C. Holman[8]

[1]Dip. Chimica, Univ. Firenze; [2] INFN, Firenze; [3] Dip. Fisica e Astr., Univ. Firenze; [4]Inst. Environ. Assess.-Water Res.(IDAEA-CSIC), Barcelona, Spain; [5]Arpa Lombardia Milano; [6]Environment Dept., Aveiro Univ, Portugal; [7]Env. Radio. Lab, NCSR Demokritos, Attiki, Greece; [8]Geogr., Earth & Env. Sci., Birmingham Univ., Birmingham, UK

11.40 – 12.00 **AMB-1** *SIZE RESOLVED METAL DISTRIBUTION IN THE PM MATTER OF THE CITY OF TURIN (ITALY)*

V. Maurino[1], M. Malandrino[1], M. Casazza[2], O. Abollino[1], C. Minero[1]

[1]Università degli Studi di Torino, Dipartimento di Chimica, Torino, Italy; [2]University 'Parthenope' of Napoli, Department of Science and Technologies, Napoli, Italy

12.00 – 12.20 **AMB-2** *CHEMICAL CHARACTERIZATION OF COARSE AND FINE FRACTION OF PM SAMPLES OF A RURAL SITE OF SOUTH ITALY*

A. Genga[1], B. Introna[1], M. Siciliano[1], T. Siciliano[2], C. Malitesta[1]

[1]Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Lecce, Italy; [2]Dipartimento di Beni Culturali, Università del Salento, Lecce, Italy.

12.20 – 12.40 **AMB-3** *SUPRAMOLECULAR DETECTION OF BTEX IN AIR: FROM SPME COATINGS TO MINIATURIZED MEMS SENSORS*

F. Bianchi, N. Riboni, F. Bertani, E. Dalcanale, M. Careri

Dipartimento di Chimica, Università di Parma.

12.40 – 13.00 **AMB-4** DETERMINATION OF CYANIDE IN SOILBY PENTAFLUOROBENZYL ALKYLATION AND GC/MS ANALYSIS

B. Campanella[1,2], L. Biancalana[1], M. Onor[2], E. Bramanti[2], A. D'Ulivo[2], Z. Mester[3], E. Pagliano[3]

[1]Istituto di Chimica dei Composti Organometallici - UOS di Pisa, Consiglio Nazionale delle Ricerche (CNR), Pisa; [2]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, [3]National Research Council of Canada, 1200 Montreal Road, Ottawa, Canada

Sessione Parallela: **Bioanalitica e Omics 1 -** ***Sala "Jonia"***

Chairman: ***Aldo Lagana***

11.10 – 11.40 **KN2** *RECENT TRENDS IN ANALYSIS OF BIOACTIVE PEPTIDES IN FOOD MATRICES*

A.L. Capriotti

Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", Roma

11.40 – 12.00 **BIO-1** *PREPARATION OF NEW COMPOSITE MATERIALS FOR PHOSPHOPEPTIDE ENRICHMENT IN SHOTGUN PHOSPHOPROTEOMICS*

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

Dipartimento di Chimica - Università degli Studi di Roma "La Sapienza", Rome, Italy

12.00 – 12.20 **BIO-2** *SOIL METAPROTEOMICS: LC/HRMS-BASED ANALYTICAL STRATEGY FOR THE STUDY OF MICROBIAL FUNCTIONS IN THE RHIZOSPHERE OF PLANTS FROM SERPENTINE SOIL*

M. Mattarozzi[1], M. Manfredi[2], B. Montanini[3], F. Gosetti[2], A.M. Sanangelantoni[3], E. Marengo[2], G. Visioli[3], M. Careri[1]

[1]Dipartimento di Chimica, Università degli Studi di Parma; [2]Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, Alessandria; [3]Dipartimento di Bioscienze, Università degli Studi di Parma

12.20 – 12.40 **BIO-3** *EVALUATION OF OBETICHOLIC ACID PHARMACOKINETICS, BIODISTRIBUTION AND METABOLISM IN DECOMPENSATED LIVER CIRRHOTIC RATS BY HPLC-ESI-MS/MS*

A. Roda[1], R. Aldini[2], P. Franco[1], M. Cont[3], L. Maroni[4], L. Adorini[5]

[1]Dipartimento di Chimica, Università di Bologna; [2]Dipartimento di Farmacia e Biotecnologie, Università di Bologna; [3]INBB, Istituto Nazionale Biostrutture e Biosistemi, Roma, [4]Dipartimento DIMES, Università di Bologna; [5]Intercept Pharmaceuticals, New York

12.40 – 13.00 **BIO-4** *MULTICOLOURS GOLD NANOPARTICLES FOR IMMUNOCHROMATOGRAPHIC STRIP TEST*

F. Di Nardo, L. Anfossi, C. Giovannoli, G. Spano, C. Baggiani

Dipartimento di Chimica, Università degli Studi di Torino

Sessione Parallela: **Sensori 1 -** ***Sala "Etna"***

Chairman: ***Renato Seeber***

11.10 – 11.40 **KN3** *ALLOSTERIC CONTROLLED DNA-BASED NANODEVICES FOR BIOSENSING APPLICATIONS*

A. Idili, A. Amodio, M. Rossetti, G. Palleschi, A.V. Belisle, K. Plaxco, F. Ricci, A. Porchetta[1]

[1]Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Tor Vergata, Roma, Italia; [2]Department of Chemistry and Biochemistry, University of California Santa Barbara, CA, USA; [3] Departement de Chimie, Universit de Montral, Quebec (Canada).

11.40 – 12.00 **SENSO-1** *PRESS-PRINTED CONDUCTIVE CARBON BLACK NANOPARTICLES FILMS FOR MOLECULAR DETECTION AT THE MICROSCALE*

F. Della Pelle[1,2], L. Vázquez[3], M. Del Carlo[2], M. Sergi[2], D. Compagnone[2], A. Escarpa[1]

[1]Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, Faculty of Biology, Environmental Sciences and Chemistry, University of Alcalá, Madrid, Spain; [2]Faculty of Bioscience and Technology for Food, Agriculture and Environment University of Teramo, Teramo, Italy; [3]Institute of Materials Science of Madrid (CSIC), Madrid, Spain

12.00 – 12.20 **SENSO-3** *A MODULAR MECHANISM TO REGULATE THE AFFINITY OF NUCLEID-ACID TARGET-RESPONSIVE NANOSWITCHES*

E. Del Grosso**,** A. Idili, A. Porchetta, G. Palleschi, F. Ricci.

Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma "Tor Vergata", Roma

12.20 – 12.40 **SENSO-4** *AMPEROMETRIC GENOSENSOR ENHANCED BY DENDRIMER-LINKED PNA PROBES: COMPETITIVE VS NONCOMPETITIVE APPROACH*

M. Giannetto, S. Fortunati, A. Rozzi, M. Mattarozzi, A. Manicardi, R. Corradini, M. Careri

Dipartimento di Chimica, Università degli Studi di Parma

14.00-15.00 **Sessione POSTER: SENSO, SEPA, SPETTRO, EQUI**

Sessione Parallela **Equilibri in Soluzione e Speciazione - *Sala "Jonia"***

Chairman: ***Silvio Sammartano***

15.00 – 15.30 **KN4** *SPECIATION IN SOLUTION: IS IT WORTH DOING IT?*

G. Arena

Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Italy

Chairman: ***Pier Giuseppe Daniele***

15.30 – 15.50 **EQUI-1** *NEW MIMOSINE – BASED PEPTIDE AS CHELATING AGENT FOR MEDICAL USE*

J.I. Lachowicz[1], V.M. Nurchi[1], G. Crisponi[1], E. Randaccio[1], Z. Szewczuk[2], R. Bachor[2], P. Stefanowicz[2], X. Lopez[3], J. I. Mujika[3], G. Dalla Torre[3], M.A. Zoroddu[4], M. Peana[4], S. Medici[4]

[1]Dept. of Chemical and Geological Sciences, University of Cagliari, Monserrato, Italy; [2]Faculty of Chemistry, University of Wroclaw, Wroclaw, Poland; [3]Kimika Fakultatea, Euskal Herriko Unibertsitatea, Donostia, Spain; [4]Dept. of Chemistry and Pharmacy, University of Sassari, Italy

15.50 – 16.10 **EQUI-2** *CHEMICAL MODELS FOR THE INTERPRETATION OF ACID/BASE CHEMISTRY AND COMPLEXATION CAPABILITY OF TANNIC ACID*

S. Berto**,** M. Ginepro, V. Schettini, P. G Daniele

Dipartimento di Chimica, Università di Torino

16.10 – 16.30 **EQUI-3** *RHENIUM(I) TRICARBONYL COMPLEXES WITH AMINOACIDS IN AQUEOUS SOLUTION*

G. De Tommaso[1]**,** M. Iuliano[1], L. De Rosa[2], G. Malgieri[3], R. Fattorusso[3,5], A. Romanelli[4,5], L. D. D'Andrea[2,5], C. Isernia[3,5]

[1]Department of Chemical Sciences, University of Naples "Federico II", Naples (Italy); [2]Institute of Biostructure and Bioimages CNR Naples (Italy);[3]Department of Environmental Science and Technologies, Biological and Pharmaceutical, Second University of Naples, Caserta (Italy);

[4]Department of Pharmacy, University of Naples "Federico II", Naples (Italy);[5]Interuniversity Research Centre on Bioactive Peptides, Naples (Italy)

16.30 – 16.50 Coffee Break

16.50 – 17.10 **EQUI-4** *3-HYDROXY-4-PIRIDINONE DERIVATIVES: SYNTHESIS, ACID - BASE PROPERTIES AND INTERACTIONS WITH Al^{3+}*

K. Chand[1], R. M. Cigala[2], A. Irto[2], F. Crea[2], C. De Stefano[2], S. Sammartano[2], M. A. Santos[1]

[1]Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Portugal; [2]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università degli Studi di Messina

17.10 – 17.30 **EQUI-5** *BRANCHED PEPTIDES AS NEW Cu(II) CHELATING AGENTS MIMICKING METALLOENZYME BINDING SITES*

M. Remelli,[1] R. Guerrini,[1] N. Marchetti,[1] M. Perinelli,[2] M. Tegoni[2]

[1]Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Ferrara; [2]Dipartimento di Chimica, Università degli Studi di Parma

17.30 – 17.50 **EQUI-6** *STABILITY CONSTANTS OF ALUMINIUM(III) COMPLEXES WITH CAFFEIC, FERULIC AND p-COUMARIC ACIDS IN AQUEOUS SOLUTION*

E. Furia, A. Beneduci, R. Elliani, A. Tagarelli

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria

17.50 – 18.10 **EQUI-7** *HYPCAL, A VERSATILE TOOL FOR THE DETERMINATION OF STANDARD REACTION ENTHALPY AND BINDING CONSTANT VALUES FROM CALORIMETRIC DATA*

C. Sgarlata[1], C. Bonaccorso[1], M. Volkova[2], P. Gans[3], G. Arena[1]

[1]Dipartimento di Scienze Chimiche, Università degli Studi di Catania; [2]Ivanovo State University of Chemistry and Technology, Ivanovo, Russia; [3]University of Leeds, U.K. (retired)

Sessione Parallela: **Scienza delle Separazioni -** ***Sala "Naxos Alcantara"***

Chairman: ***Luigi Mondello***

15.00 – 15.30 **KN5** *UTILIZATION OF SPME-LC-MS PLATFORM FOR PROFILING OF METABOLIC CHANGES IN ORGANS PRIOR TRANSPLANTATION*

B. Bojko,[1,2], I. Stryjak[1], K. Gorynski[1], G. A. Gomez-Rios[2], E. Cudjoe[2], and J. Pawliszyn[2]

[1]Department of Pharmacodynamic and Molecular Pharmacology, Faculty of Pharmacy, Nicolaus Copernicus University, Bydgoszcz, Poland; [2]Department of Chemistry, University of Waterloo, Canada

15.30 – 15.50 **SEPA-1** *TIMING IN ANALYTICAL PYROLYSIS: Py(HMDS)-GC/MS OF GLUCOSE AND CELLULOSE USING ON-LINE MICRO REACTION SAMPLER*

M. Mattonai, D. Tamburini, E. Ribechini, M.P. Colombini

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Italy

15.50 – 16.10 **SEPA-2** *COMBINATION OF CAPILLARY ELECTROPHORESIS, QUALITY BY DESIGN, NMR AND MOLECULAR MODELING FOR IMPURITY PROFILING: DEFINITION OF THE DESIGN SPACE AND INVESTIGATION OF INTERMOLECULAR AFFINITIES, COMPLEXATION AND SEPARATION MECHANISMS*

S. Furlanetto[1], S. Orlandini[1], B. Pasquini[1], F. Melani[3], C. Caprini[1], M. Innocenti[2], M. Del Bubba[2]

Dipartimento di Chimica "U. Schiff", Università degli Studi di Firenze, [1]Via U. Schiff 6 – [2]Via Della Lastruccia 3 – 50019 Sesto Fiorentino, Firenze; [3]Dipartimento di NEUROFARBA, Università degli Studi di Firenze, Sesto Fiorentino, Firenze

16.10 – 16.30 **SEPA-3** *MASS TRANSFER IN NEW CHIRAL STATIONARY PHASES DEVELOPED ON CORE-SHELL AND SUB-2μm FULLY POROUS PARTICLES FOR ULTRAFAST CHIRAL SEPARATIONS*

A. Cavazzini[1], M. Catani[1], L. Pasti[1], F. Gasparrini[2], O. Ismail[2]

[1]Department of Chemistry and Pharmaceutical Sciences (University of Ferrara), Italy; [2]Dipartimento di Chimica e Tecnologie del Farmaco (University of Rome, La Sapienza), Italy

16.30 – 16.50 Coffee Break

16.50 – 17.10 **SEPA-4** *HIGH EFFICIENCY MULTIDIMENSIONAL GAS CHROMATOGRAPHY COUPLED TO ISOTOPE RATIO MASS SPECTROMETRY AND QUADRUPOLE MASS SPECTROMETRY SIMULTANEOUS DETECTION*

D. Sciarrone[1], A. Schepis[1], L. Mondello[1,2,3]

[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina, Polo Annunziata, Messina, Italia; [2]Chromaleont s.r.l., c/o Università di Messina, Messina, Italia; [3]Università Campus Bio-medico di Roma, Roma, Italia

17.10 – 17.30 **SEPA-5** *A QUALITY-BY-DESIGN OPPROACH FOR THE DEVELOPMENT OF RP-HPLC METHODS FOR THE ANALYSIS OF PLANT SECONDARY METABOLYTES*

D. Corradini[1], L. De Gara[2], I. Nicoletti[1], F. Orsini[2].

[1]National Research Council, Institute of Chemical Methodologies, Area della Ricerca di Roma 1, Montelibretti, Rome, Italy; [2]University Campus Bio-Medico of Rome, Rome, Italy.

17.30 – 17.50 **SEPA-6** *DEVELOPMENT AND MULTIVARIATE OPTIMIZATION OF A MEPS-PTV-GC-MS/MS METHOD FOR ORGANOPHOSPHATE FLAME RETARDANTS ANALYSIS IN ENVIRONMENTAL AQUEOUS MATRICES*

R. Elliani[1], A. Naccarato[2], G. Sindona[1], A. Tagarelli[1]

[1]Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Arcavacata di Rende (CS); [2]CNR-Istituto sull'Inquinamento Atmosferico, Divisione di Rende, Università della Calabria-Polifunzionale - Arcavacata di Rende (CS)

17.50 – 18.10 **SEPA-7** *DETERMINATION OF PERFLUORO-ALKYL ACIDS IN DIFFERENT WATER MATRICES BY MEANS OF DIRECT INJECTION LC-MS/MS ANALYSIS*

M. Del Bubba[1], L. Ciofi[1], L. Renai[1], L. Checchini[1], A. Falai[2], D. Santianni[2], E. Coppini[3], D. Fibbi[3], S. Furlanetto[1]

[1]Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Sesto Fiorentino, Firenze; [2]Publiacqua S.p.A., Firenze; [3]G.I.D.A. S.p.A., Prato

Sessione Parallela: **Spettroscopia Analitica - *Sala "Etna"***

Chairman: ***Giuseppe Spoto***

15.00 – 15.30 **KN6** *SURFACE XPS STUDY OF ION EXCHANGE IN ERIONITE*

M. Fantauzzi[1], A. Pacella[2]

[1]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Monserrato (CA); [2]Dipartimento di Scienze della Terra, Sapienza Università Roma, Roma

15.30 – 15.50 **SPETTRO-1** *ADVANCED OPERANDO X-RAY ANALYTICAL TECHNIQUES: CHARACTERIZATION OF NEW MATERIALS FOR SOLAR ENERGY CONVERSION*

A. Giaccherini[1], W. Giurlani[1], B. Pasquini[1], F. Capolupo[1], R.A. Picca[2], R. Felici[3], F. Carlà[4], N. Cioffi[2], S. Furlanetto[1], A. Lavacchi[5], F. Di Benedetto[6] and M. Innocenti[1,5]

[1]Dipartimento di Chimica, Università Degli Studi di Firenze, Firenze; [2] Dipartimento di Chimica, Università Degli Studi di Bari "Aldo Moro", Bari; [3] SPIN – CNR, Roma, Italy;[4] ESRF, Grenoble, Cedex, France;[5] ICCOM – CNR, Firenze, Italy;[6] Dipartimento di Scienze della Terra, Università Degli Studi di Firenze, Firenze

15.50 – 16.10 **SPETTRO-2** *CHEMICAL VAPOR GENERATION ATOMIC SPECTROMETRY FOR CADMIUM DETERMINATION AT TRACE LEVEL: SOME RECENT DEVELOPMENTS*

E. Pitzalis, D. Angelini, M.C. Mascherpa, A. D'Ulivo

Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organo Metallici, Pisa

16.10 – 16.30 **SPETTRO-3** *TRIBOLOGICALLY-INDUCED STRUCTURAL EVOLUTION OF SILICON OXIDE-DOPED HYDROGENATED CARBON: A SURFACE-ANALYTICAL INVESTIGATION*

F. Mangolini[1], K.D. Koshigan[2], M.H. Van Benthem[3], J.A. Ohlhausen[3], J.B. McClimon[4], J. Hilbert[5], J.R. Lukes[5], J. Fontaine[2], R.W. Carpick[5]

[1] Institute of Functional Surfaces, School of Mechanical Engineering, University of Leeds, UK; [2]Laboratoire de Tribologie et Dynamique des Systèmes, Ecole Centrale de Lyon, France; [3]Sandia National Laboratories, Albuquerque, New Mexico, USA; [4]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, USA; [5]Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, USA

16.30 – 16.50 Coffee Break

Chairman: ***Antonella Rossi***

16.50 – 17.10 **SPETTRO-4** *SYNTHESIS OF NANOANTIMICROBIALS BY LASER ABLATION IN LIQUIDS AND THEIR APPLICATION TO FOOD PACKAGING*

M.C. Sportelli[1,2], A. Ancona[2], R.A. Picca[1], A. Volpe[2,3], P.M. Lugarà[2,3], N. Cioffi[1]

[1]Chemistry Department, University of Bari, Italy; [2]IFN-CNR, Physics Department, University of Bari, Italy; [3]Physics Department, University of Bari, Italy

17.10 – 17.30 **SPETTRO-5** *RECENT APPLICATIONS OF PLASMONIC NANOMATERIALS AND THEIR COMPOSITES: FROM LOCALIZED SURFACE PLASMON RESONANCE (LSPR) TO COLORIMETRIC DETECTION FOR BIOANALYSIS*

S. Scarano[1,], M. Bonini[1], M.G. Manera[2], A. Colombelli[2], R. Rella[2], and M. Minunni[1]

[1]Department of Chemistry 'Ugo Schiff' and CSGI, University of Florence, Sesto Fiorentino, Firenze, Italy; [2]CNR-IMM-Institute for Microelectronic and Microsystems, Unit of Lecce, Lecce, Italy

17.30 – 17.50 **SPETTRO-6** *AN XPS STUDY OF ELECTROCHEMICALLY DEPOSITED SULPHIDE SEMICONDUCTORS FOR THIN FILM PHOTOVOLTAICS*

R.A. Picca[1], A. Giaccherini[2], F. Di Benedetto[3], M. Innocenti[2], N. Cioffi[1]

[1]Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Bari; [2]Dipartimento di Chimica, Università degli Studi di Firenze, Sesto Fiorentino (FI); [3]Dipartimento di Scienze della Terra, Università degli Studi di Firenze

17.50 – 18.10 **SPETTRO-7** *FLAT BIMETALLIC MICRO- AND NANO-PATTERNS FOR CALIBRATION OF SURFACE ANALYSIS INSTRUMENTS*

C. Passiu[1], A. Rossi[1,2], W. Unger[3], N. D. Spencer[1]

[1]Laboratory for Surface Science and Technology, Department of Materials, ETH Zurich, Switzerland; [2]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Cittadella Universitaria di Monserrato, Cagliari; [3]BAM Federal Institute for Materials Research and Testing, Berlin, Germany

18.30 – 20.00 Assemblea plenaria della Divisione (Consegna Medaglie) ***Sala "Naxos Alcantara"***

Martedì 20 Settembre 2016

Sala "Naxos Alcantara"

09.00 – 09.45 Conferenza Plenaria **PL2 –** Chaiman: ***Giuseppe Palleschi***

Lo Gorton (University of Lund, Sweden)

DIRECT ELECTRON TRANSFER BETWEEN SUGAR OXIDISING ENZYMES AND ELECTRODES AS BASIS FOR 3RD GENERATION BIOSENSORS/BIOANODES

Sessione Parallela: **Ambiente 2 - *Sala "Naxos Alcantara"***

Chairman: ***Andrea Tapparo***

10.10 – 10.30 **AMB-5** *A MULTI-TECHNIQUE APPROACH FOR THE CHARACTERIZATION OF PM 2.5 DUE TO BIOMASS COMBUSTION*

P. Fermo[2], D. Atzei[1], M. Fantauzzi[1], L. Corbella[2], R. Vecchi[3], G. Valli[3], A. Rossi[1]

[1]Dipartimento di Scienze Chimiche e Geologiche - Università di Cagliari; [2]Dipartimento di Chimica, Università degli Studi di Milano; [3]Dipartimento di Fisica, Università degli Studi di Milano

10.30 – 10.50 **AMB-6** *BIOMARKERS IN LACUSTRINE SEDIMENT CORES FOR RECONSTRUCTING EARLY HUMAN ACTIVITY AND FIRE HISTORY*

D. Battistel[1,2], N.M. Kehrwald[3], T. Kirchgeorg[1], E. Argiriadis[1], A. Callegaro[1], C. Barbante[1,2]

[1]Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Cà Foscari Venezia; [2]Institute for the Dynamics of Environmental Processes, IDPA-CNR, Mestre, Venezia; [3]U.S. Geological Survey, Geosciences and Environmental Change Science Center, Lakewood, USA

10.50 – 11.10 **AMB-7** *MAJOR AND MINOR ELEMENTS IN THERMOCHEMICAL CONVERSION OF BIOMASS*

J. Tafur-Marinos, S. Barbero, M. Ginepro, V. Zelano

Dipartimento di Chimica, Università degli Studi di Torino

11.10 – 11.30 **AMB-8** *TRACE AND RARE EARTH ELEMENTS IN PM_{10} COLLECTED AT NY-ÅLESUND (SVALBARD ISLANDS, ARCTICA)*

M. Malandrino[1], O. Abollino[1], A. Giacomino[2], S. Buoso[1], E. Conca[1], R. Udisti[3]

[1]Dipartimento di Chimica, Università degli Studi di Torino; [2]Dipartimento di Scienze e Tecnologia del Farmaco, Università degli Studi di Torino; [3]Dipartimento di Chimica, Università degli Studi di Firenze

11.30 – 11.50 **Coffee Break**

Chairman: ***Giuseppe Scarponi***

11.50-12.10 **AMB-9** *PRIMARY PRODUCTION, SEA ICE MELTING, AND BIOGENIC AEROSOL IN THE ARCTIC*

S. Becagli[1], L. Lazzara[2], C. Marchese[3], S.E. Ascanius[4], M. Cacciani[5], L. Caiazzo[1],C. Di Biagio[6,7], T. Di Iorio[6], A. di Sarra[6], P. Eriksen[8], F. Fani[2], F. Giardi[1], D. Meloni[6], G. Muscari[9], G. Pace[6], M. Severi[1], R. Traversi[1], R. Udisti[1].

[1]Department of Chemistry, University of Florence, Italy; [2]Department of Biology, University of Florence, Italy; [3]Département de Biologie, Chimie et Géographie, Université du Québec à Rimouski, Québec, Canada; [4]Danish Meteorological Isntitute, Qaanaaq, Greenland; [5]Physics Department, Sapienza University of Rome, Italy; [6]ENEA, Laboratory for Earth Observations and Analyses, Rome, Italy; [7]LISA, UMR CNRS 7583, Université Paris Est Créteil et Université Paris Diderot Institut Pierre Simon Laplace Créteil, France; [8]Danish Meteorological Institute, Copenhagen, Denmark; [9] Istituto Nazionale di Geofisica e Vulcanologia, INGV, Rome, Italy.

12.10 – 12.30 **AMB-10** *EVIDENCE OFTHE LASCHAMP GEOMAGNETIC EXCURSION IN THE NITRATE RECORD FROM EPICA-DOME C ICE CORE*

R. Traversi[1], S. Becagli[1], S. Poluianov[2], M. Severi[1], S.K. Solanki[3,4], I.G. Usoskin[2,5], R. Udisti[1]

[1]Dipartimento di Chimica"Ugo Schiff", Università di Firenze; [2]ReSoLVE Center of Excellence, Faculty of Sciences, University of Oulu, Finland; [3]Max-Planck-Institut für Sonnensystemforschung, Justus-von-Liebig-Weg 3, Göttingen, Germany; [4]School of Space Research, Kyung Hee University, Yongin, Gyeonggi, South Korea; [5]Sodankylä Geophysical Observatory, Oulu unit, University of Oulu, Finland.

12.30 – 12.50 **AMB-11** *FIRST MEASUREMENTS OF TRACE METALS IN THE ATMOSPHERIC AEROSOL OF CENTRAL ANTARCTICA AT DOME C (CONCORDIA STATION)*

C. Mantini**,** C. Truzzi, A. Annibaldi, S. Illuminati, G. Scarponi

Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, Ancona

12.50 – 13.10 **AMB-12** *RECOVERING PALEO-RECORDS FROM ANTARCTIC ICE-CORES BY COUPLING A CONTINUOUS MELTING DEVICE AND FAST ION CHROMATOGRAPHY.*

M. Severi, S. Becagli, L. Caiazzo, F. Giardi, M. Marconi, R. Traversi, R. Udisti.

Dipartimento di Chimica "Ugo Schiff", Università di Firenze.

Sessione Parallela: **Bioanalitica 2 -** ***Sala "Jonia"***

Chairman: ***Aldo Roda***

10.00 – 10.30 **KN7** *A SIMPLE SMARTPHONE BIOSENSOR BASED ON SILICA FUNCTIONALIZED NANOPARTICLES DOPED WITH NEW THERMOCHEMILUMINESCENT ACRIDINE-1,2-DIOXETANE DERIVATIVES AS UNIVERSAL REAGENT-LESS LABEL FOR BIOASSAYS*

M. Mirasoli, L.A. Andronico, D. Calabria, A. Quintavalla, M. Lombardo, C. Trombini, A. Roda

Department of Chemistry ''Giacomo Ciamician'', Alma Mater Studiorum, University of Bologna

10.30 – 10.50 **BIO-5** *BINDING PROPERTIES OF ENZYME TRACERS TO MOLECULARLY IMPRINTED POLYMERS AS MIMICS OF ANTIBODIES*

C. Baggiani, G. Spano, C. Giovannoli, F. Di Nardo, L. Anfossi

Dipartimento di Chimica, Università degli Studi di Torino

10.50 – 11.10 **BIO-6** *ELEMENTAL CONTENT IN HUMAN PLACENTA: THE EFFECT OF GESTATIONAL DIABETES MELLITUS AND OF OTHER FACTORS*

M. Roverso,[1,2] F. Lorigiola[1], V. Di Marco[1], D. Badocco[1], P. Pastore[1], S. Visentin[3]

[1]Dipartimento di Scienze Chimiche, Università di Padova; [2]Dipartimento di Medicina, Università di Padova; [3]Dipartimento di Salute della Donna e del Bambino, Università di Padova

11.10 – 11.30 **BIO-7** *THE EFFECT OF EXERCISE ON SALIVARY LACTATE, ALPHA-AMYLASE AND URIC ACID IN HEALTHY VOLUNTEERS*

T. Lomonaco[1], S. Ghimenti[1], E. Bramanti[2], D. Biagini[1], F. G. Bellagambi[1], M. Onor[2], R. Fuoco[1], F. Di Fancesco[1]

[1]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa; [2]Istituto di Chimica dei Composti Organometallici, Consiglio Nazionale delle Ricerche, Pisa

11.30 – 11.50 Coffee Break

11.50 – 12.10 **BIO-8** *PRENATAL SCREENING USING MS-BASED PROTEOMIC APPROACH ON COELOMIC FLUID: A PILOT STUDY*

D. Aiello[1]**,** F. Mazzotti[1]**,** A. Giambona[2], F. Leto[2], C. Passarello[2], G. Damiani[3], V. Cigna[3], G. Schillaci[3], A. Maggio[2], A. Napoli[1]

[1]Department of Chemistry and Chemical Technologies, University of Calabria; [2]Unit of Haematology for rare diseases of blood and blood-forming organs, Regional Reference Laboratory for screening and prenatal diagnosis of hemoglobinopathies, Palermo; [3]Unit of Prenatal Diagnosis, Hospital Villa Sofia Cervello, Palermo

12.10 – 12.30 **BIO-9** *DETERMINATION OF BIOMARKERS IN BREATH AND SALIVA FOR MONITORING HEART FAILURE PATIENTS*

F.G. Bellagambi[1], T. Lomonaco[1], S. Ghimenti[1], F. Di Francesco[1], M. Marzilli[2], R. Fuoco[1]

[1]Dipartimento di Chimica, Università di Pisa;[2] Dipartimento di Patologia Chirurgica, Medica, Molecolare e dell'Area Critica, Università di Pisa;[3]Dipartimento di Patologia Chirurgica, Medica, Molecolare e dell'Area Critica, Università di Pisa

12.30 – 12.50 **BIO-10** *MIGRATION TESTS ON MODEL ANTIBACTERIAL Ag NPs COATINGS*

D. Spanu[1], S.Recchia[1], D.Monticelli[1]

[1]Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Como

12.50 – 13.10 **BIO-11** *IN-FLIGHT MONITORING SALIVARY STRESS BIOMARKERS ON THE INTERNATIONAL SPACE STATION USING AN ULTRASENSITIVE MICROFLUIDIC-ASSISTED CHEMILUMINESCENT LATERAL FLOW IMMUNOASSAY*

M. Zangheri[1], M. Mirasoli[1], M. Guardigli[1], L. Anfossi[2], F. Di Nardo[2], C. Giovannoli[2], C. Baggiani[2], P. Simoni[3], A. Roda[1]

[1]Dipartimento di Chimica "Giacomo Ciamician", Alma Mater Studiorum - Università di Bologna; [2]Dipartimento di Chimica, Università di Torino; [3]Dipartimento di Medicina e Chirurgia, Alma Mater Studiorum - Università di Bologna

Sessione Parallela: **Elettroanalitica + Green Chemistry -** ***Sala "Etna"***

Chairman: ***Carlo Dossi***

10.00 – 10.30 **KN8** *RECENT TRENDS IN THE EMPLOYMENT OF ELECTROCHEMICAL TECHNIQUES FOR THE CHARACTERIZATION OF CORROSION PRODUCTS OF ARCHAEOLOGICAL METALS*

F. Di Turo[1], N. Montoya[2], J. Piquero-Cilla[2], C. De Vito[1], R. Antiochia[3], F. Mazzei[3], G. Favero[3], A. Doménech-Carbó[2]

[1]Department of Earth Sciences, Sapienza University of Rome, Italy; [2] Departament de Química Analítica. Universitat de València. Burjassot (València) Spain; [3] Department of Chemistry and Drug Technologies, Sapienza University of Rome, Italy

10.30 – 10.50 **ELETTRO-1** *DIRECT ELECTRODEPOSITION OF GOLD NANOPARTICLES ONTO GLASSY CARBON ELECTRODE AS BIOFUEL CELL BIOANODE BASED ON CELLOBIOSE DEHYDROGENASE*

P. Bollella[1], R. Ludwig[3], G. Favero[1], F. Mazzei[1], Lo Gorton[2], R. Antiochia[1]

[1]Department of Chemistry and Drug Technologies, Sapienza University of Rome, Italy; [2]Department of Analytical Chemistry/Biochemistry, Lund, Sweden; [3]Department of Food Sciences and Technology, Food Biotechnology Laboratory, BOKU–University of Natural Resources and Life Sciences, Vienna, Austria

10.50 – 11.10 **ELETTRO-2** *DEPOSITION AND CHARACTERIZATION OF A COBALT HEXACYANOFERRATE NANOROD ARRAY IN A TEMPLATED ORMOSIL FILM ON AN ELECTRODE AND APPLICATION TO ELECTROCATALYSIS***.**

M. Ciabocco[1], M. Berrettoni[1], S. Zamponi[2], J. A. Cox[3]

[1]Dept of Chemistry, University of Bologna, Rimini Campus, Rimini, Italy; [2]Dept of Chemistry, University of Camerino, Italy; [3]Department of Chemistry and Biochemistry, Miami University, Oxford, USA

11.10 – 11.30 **ELETTRO-3** *VOLTAMMETRIC DETERMINATION OF IRON IN SEAWATER BY ATMOSPHERIC OXYGEN CATALYSIS IN 500 μL SAMPLES*

S. Caprara[1], C. Dossi[2], D. Monticelli[1]

[1]Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Como; [2]Dipartimento di Scienze teoriche e Applicate, Università degli Studi dell'Insubria, Varese

11.30 – 11.50 Coffee Break

11.50 – 12.10 **ELETTRO-4** *CHIRAL ELECTROANALYSIS ON ACHIRAL ELECTRODES IN "INHERENTLY CHIRAL" IONIC LIQUID MEDIA*

P.R.Mussini,[1] S. Arnaboldi,[1] A. Gennaro[2], A.A. Isse[2], V. Michali,[1], S. Rizzo,[3] F. Sannicolò[1]

[1]Dip. di Chimica, Univ. degli Studi di Milano; [2]Dip. di Scienze Chimiche, Univ. degli Studi di Padova; [3]CNR ISTM, Milano

12.10 – 12.30 **GREEN-1** *EFFICIENT HYDROGEN PRODUCTION BY g-C_3N_4: CORRELATION BETWEEN PHYSICO-CHEMICAL PARAMETERS AND VISIBLE-LIGHT PHOTOCATALYSIS*

A. Speltini[1], F. Maraschi[1], M. Sturini[1], A. Profumo[1], C. Milanese[1], L. Sangaletti[2], G. Drera[2], M. Patrini[3], G. Guizzetti[3], L. Malavasi[1,4]

[1]Dipartimento di Chimica, Università di Pavia, Italy; [2]I-LAMP, Dipartimento di Matematica e Fisica, Università Cattolica del Sacro Cuore, Brescia, Italy; [3]CNISM, Università di Pavia, Italy; [4]Dipartimento di Chimica, Università di Pavia, e INSTM, Pavia, Italy

12.30 – 12.50 **GREEN-2** *ENERGY RETURNED ON ENERGY INVESTED (EROEI) IN ANALYTICAL CHEMISTRY*

M. Innocenti[1,3], A. Giaccherini[1], F. Di Benedetto[2], A. Lavacchi[3], H.A. Miller[3], N. Cioffi[4], R.A. Picca[4] and F. Vizza[3].

[1]Dipartimento di Chimica, Università degli Studi di Firenze; [2]Dipartimento di Scienze della Terra, Università di Firenze; [3]Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR and INSTM Consortium, Sesto F.no, (Florence); [4]Dipartimento di Chimica, Università degli Studi di Bari.

14.00 – 15.00 **SESSIONE POSTER: GREEN, AMB, BC, BIO**

15.00 – 16.00 Assemblee dei gruppi interdivisionali

16.15 **Visita guidata a Taormina (meeting point Atahotel Naxos Beach)**

19.30 **Partenza da Taormina per Forza d'Agrò trattoria tipica "Osteria Agostiniana"**

Mercoledì 21 Settembre 2016

Sala "Naxos Alcantara"

09.00 – 09.45 Conferenza Plenaria **PL3 –** Chairman: ***Tommaso Cataldi***

Gerhard Liebisch (University Hospital Regensburg, Germany)

LIPIDOMICS - FROM QUANTIFICATION TO CLINICAL APPLICATION

Sessione Parallela: **Beni Culturali 1 -** ***Sala "Naxos Alcantara"***

Chairman: ***Luigia Sabbatini***

10.00 – 10.30 **KN9** *NEW FRONTIERS IN APPLICATION OF FTIR MICROSCOPY FOR THE CHARACTERIZATION OF CULTURAL HERITAGE MATERIALS*

R. Mazzeo, S. Prati, G. Sciutto, I. Bonacini

Dipartimento di Chimica "G. Ciamician", Laboratorio diagnostico di microchimica e microscopia (M2ADL) per i beni culturali, Università di Bologna – Campus Ravenna, (Italia)

10.30 – 10.50 **BC-1** *MODERN INKS ANALYSIS AND CONSERVATION PROBLEMS: CASE STUDIES*

G. Germinario[1], I. D. van der Werf[1,2], A. Mirabile[3], L. Sabbatini[1,2]

[1]Dipartimento di Chimica, Università degli Studi di Bari, Italy; [2]Centro interdipartimentale "Laboratorio di ricerca per la diagnostica dei Beni Culturali", Università degli Studi di Bari Aldo Moro, Italy; [3]Paper conservator, 11 rue de Bellefond, Paris, France

10.50 – 11.10 **BC-2** *APPLICATION OF A REAL TIME MONITORING TOOL WITH ELECTROCHEMICAL DETECTION: A CASE STUDY*

L. Micheli[1], C. Mazzuca[1], S. Dominijanni [2], S. Puteo [2], S. Sotgiu[2], S. Iannuccelli[2], A. Palleschi[1], G. Palleschi[1]

[1] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Rome, Italy; [2]Istituto centrale per il restauro e la conservazione del patrimonio archivistico e librario, Rome, Italy

11.10 – 11.30 Coffee Break

11.30 – 11.50 **BC-3** *THE COLOURS OF THE "COPTIC" TEXTILESAT THE MUSEO EGIZIO DI TORINO*

M.Gulmini[1], A. Idone[1], P. Davit[1], E. Diana[1], F. Natale[1], F. Dal Bello[2], M. Borla[3], C. Greco[4]and M. Aceto[5]

[1]Dipartimento di Chimica, Università degli Studi di Torino; [2]Dipartimento di Biotecnologie Molecolari e Scienze per la Salute, Università degli Studi di Torino; [3]Soprintendenza Archeologia del Piemonte, Torino; [4]Museo Egizio di Torino; [5]Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale &Centro Interdisciplinare per lo Studio e la Conservazione dei Beni Culturali (CenISCo), Università degli Studi del Piemonte Orientale

11.50 – 12.10 **BC-4** *CHARACTERIZATION OF CORROSION PRODUCTS OF ROMAN BRONZE COINS USING TRADITIONAL (SEM-EDS, XRD) AND ELECTROCHEMICAL (VMP, EIS) TECHNIQUES*

F. Di Turo[1], N. Montoya[2], J. Piquero-Cilla[2], C. De Vito[1], R. Antiochia[3], F. Mazzei[3], G. Favero[3], A. Doménech-Carbó[2]

[1] Department of Earth Sciences, Sapienza University of Rome, Italy; [2] Departament de Química Analítica. Universitat de València. Burjassot (València) Spain; [3] Department of Chemistry and Drug Technologies, Sapienza University of Rome, Italy

12.10 – 12.30 **BC-5** *CHARACTERIZATION OF BRASS ALLOYS AGED AT OPEN CIRCUIT POTENTIAL IN NEUTRAL SOLUTIONS BY XPS and XAES.*

F. Cocco[1], B. Elsener[1,2], M. Fantauzzi[1], A. Rossi[1]

[1]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Campus di Monserrato Cagliari – Italy; [2]ETH Zurich, Institute for Building Materials, ETH Hönggerberg, CH-8093 Zurich

12.30 – 12.50 **BC-6** *TECHNOLOGY AND PROVENANCE OF THE MAIOLICA SCULPTURES FROM OSTRA VETERE AND ANCONA (MARCHE, ITALY)*

M. L. Amadori[1], P. Fermo[2]

[1]University of Urbino, Department of Pure and Applied Sciences; [2]University of Milan, Department of Chemistry

12.50 – 13.10 **BC-7** *CHEMILUMINESCENCE LATERAL FLOW IMMUNOASSAY FOR A NEW GENERATION OF PORTABLE PAINT ANALYSIS KITS*

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

[1]Microchemistry and Microscopy Art Diagnostic Laboratory Department of Chemistry "G. Ciamician", University of Bologna; [2] Department of Chemistry "Giacomo Ciamician", University of Bologna; [3] Department of Chemistry, University of Torino

Sessione Parallela: **Sensori 2 - *Sala "Jonia"***

Chairman: ***Giovanna Marrazza***

10.00 – 10.30 **KN10** *NANOSTRUCTURED ELECTROCHEMCIAL BIOSENSING PLATFORMS FOR NUCLEIC ACID DETECTION*

I. Palchetti

Dipartimento di Chimica, Università degli Studi di Firenze, Sesto Fiorentino, Firenze

10.30 – 10.50 **SENSO-5** *MIP NANOPARTICLES AS ASCORBIC ACID SCAVENGER IN ELECTROCHEMICAL MEASUREMENTS*

R. Rapini[1], F. Canfarotta[2], G. Marrazza[1], S. Piletsky[2]

[1]Department of Chemistry "Ugo Schiff", University of Firenze, Sesto Fiorentino (FI), Italy; [2]Chemistry department, Leicester University, Leicester LE1 7RH, UK

10.50 – 11.10 **SENSO-6** *IMPROVED DIRECT ELECTRON TRANSFER COMMUNICATION BETWEEN CELLOBIOSE DEHYDROGENASE AND A GOLD ELECTRODE MODIFIED WITH A RIGID SELF-ASSEMBLED MONOLAYER AND GREEN METAL NANOPARTICLES: THE ROLE OF AN ORDERED NANOSTRUCTURATION*

P. Bollella[1], L. Gorton[2], G. Favero[1], F. Mazzei[1], R. Antiochia[1]

[1]Department of Chemistry and Drug Technologies, Sapienza University of Rome Italy; [2]Department of Analytical Chemistry/Biochemistry, Lund, Sweden

11.10 – 11.30 Coffee Break

11.30 – 11.50 **SENSO-8** *CONDUCTIVE POLYMER NANOCOMPOSITE BASED IMPEDIMETRIC IMMUNOSENSOR FOR 2,4-DICHLOROPHENOXY ACEDIC ACID DETECTION*

G. Fusco[1,2], C. Tortolini[1], A. D'Annibale[2], A. De Mico[2,3], R. Antiochia[1], G. Favero[1], F. Mazzei[1]

[1]Department of Chemistry and Drug Technologies, Sapienza University of Rome, Italy; [2]Department of Chemistry, Sapienza University of Rome, Italy; [3]Institute of Molecular Biology and Pathology - National Research Council, Italy

11.50 – 12.10 **SENSO-9** *THE ROLE OF PAPER IN ELECTROCHEMICAL (BIO)SENSING BREAKTHROUGH*

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

Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma "Tor Vergata"

12.10 – 12.30 **SENSO-10** *DETECTION OF DIMETHOATE IN WHEAT USING A MIP-GLASSY CARBON ELECTRODE COUPLED TO MICROEXTRACTION BY PACKED SORBENT (MEPS)*

D. Capoferri, M. Del Carlo, M. Sergi, F. Di Ottavio, D. Compagnone

Facoltà di Bioscienze e Tecnologie Agroalimentari e Ambientali, Università degli Studi di Teramo

12.30 – 12.50 **SENSO-11** *FLEXIBLE, BIOCOMPATIBLE AND DISPOSABLE pH AND TEMPERATURE SENSORS BASED ON CARBON NANO-STRUCTURED MATERIALS*

B. Melai, N. Calisi, P. Salvo, C. Paoletti, E. Herrera, V. Mollica, R. Fuoco and F. Di Francesco

Dipartimento di Chimica e Chimica Industriale, Università di Pisa

12.50 – 13.10 **SENSO-2** *NEW APPLICATIONS OF ENZYMATIC (OR NOT ENZYMATIC) DMFC DEVICES USED AS ANALYTICAL TOOLS: ANALYSIS OF PHARMACEUTICAL TINCTURES OR ACTIVE PRINCIPIA (WITH ALCOHOLIC GROUP) AND BIOLOGICAL FLUIDS*

M. Tomassetti, R. Angeloni, G. Merola, S. Marchiandi, M. Castrucci, L. Campanella.

Dipartimento di Chimica, Università di Roma "La Sapienza", Roma.

Sessione Parallela: **Spettrometria di Massa - *Sala "Etna"***

Charman: ***Tommaso Cataldi***

10.00 – 10.30 **KN11** *NATIVE AND OXIDIZED FREE FATTY ACIDS IN MUSSELS INVESTIGATED BY LIQUID CHROMATOGRAPHY-ELECTROSPRAY IONIZATION-FOURIER TRANSFORM MASS SPECTROMETRY*

I. Losito[1,2], L. Facchini[1], A. Valentini[1], T.R.I. Cataldi[1,2], F. Palmisano[1,2]

[1]Dipartimento di Chimica, [2]Centro di Ricerca Interdipartimentale SMART, Università degli Studi di Bari "Aldo Moro", Bari

10.30 – 10.50 **MS-1** *REGIOCHEMICAL ASSIGNMENT OF SULFOQUINOVOSYL-DIACYLGLYCEROLS IN PARSLEY AND SPINACH LEAVES EXTRACTS BY REVERSED-PHASE LC-ESI-MS/MS*

S. Granafei[1], P. Azzone[1], I. Losito[1,2], C.D. Calvano[1,2], F. Palmisano[1,2], T.R.I. Cataldi[1,2]

[1] Dipartimento di Chimica, [2] Centro Interdipartimentale SMART, Università degli Studi di Bari Aldo Moro, Bari

10.50 – 11.10 **MS-2** *CHROMATOGRAPHIC AND MASS-SPECTROMETRIC METHODS OPTIMIZATION FOR THE UNTARGETED ANALYSIS OF COMPLEX PHYTOCHEMICAL MIXTURES*

C. Cavaliere, G. La Barbera, R. Samperi, A. Laganà

Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", Roma

11.10 – 11.30 Coffee Break

11.30 – 11.50 **MS-3** *UHPLC COUPLED TO HIGH RESOLUTION MASS SPECTROMETRY FOR THE EVALUATION OF NON-INTENTIONALLY ADDED SUBSTANCES (NIAS) FROM FOOD CONTACT MATERIAL*

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

Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze, Parma

11.50 – 12.10 **MS-4** *STUDY OF THE TRANSFORMATION PRODUCTS OF THEV SWEETENER STEVIOSIDE BY USING HIGH RESOLUTION MASS SPECTROMETRY*

M. Sarro[1], C. Medana[2], V.A. Sakkas[3], P. Calza[1]

[1] Department of Chemistry and NIS Centre of Excellence, University of Torino; [2]Department of Molecular Biotechnology and Health Sciences, University of Torino, [3] Department of Chemistry, University of Ioannina, Ioannina, Greece

12.10 – 12.30 **MS-5** *LIQUID EI (LEI) INTERFACE: A NEW CONCEPT FOR INTERFACING LIQUID CHROMATOGRAPHY AND ELECTRON IONIZATION MASS SPECTROMETRY*

V. Termopoli, G. Famiglini, P. Palma, M. Piergiovanni, A. Cappiello.

LAB LC-MS, Dipartimento di Scienze Pure ed Applicate, Università di Urbino, Italy

12.30 – 12.50 **MS-6** *LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY METHOD FOR THE DETERMINATION OF VITAMIN K HOMOLOGUES IN BREAST MILK*

A. Gentili[1], A. Miccheli[1], P. Tomai[1], M.E. Baldassarre[2], R. Curini[1], V. Pérez-Fernández[1]

[1]Department of Chemistry, Faculty of Mathematical, Physical and Natural Science, "Sapienza" University of Rome, Italy; [2]Department of Biomedical Sciences and Human Oncology, University of Bari "Aldo Moro", Italy.

12.50 – 13.10 **MS-7** *METAL-NANOPARTICLE DECORATED SILICON NANOWIRES FOR LDI-MS APPLICATIONS*

R.A. Picca[1], M.J. Lo Faro[2], C.D. Calvano[1], B. Fazio[2], S. Trusso[2], P.M. Ossi[3], F. Neri[4], C. D'Andrea[5], A. Irrera[2], N. Cioffi[1]

[1]Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Bari; [2]IPCF-CNR, Messina; [3]Dipartimento di Energia & Center for NanoEngineered Materials and Surfaces-NEMAS, Politecnico di Milano, Italy; [4]Dipartimento di Fisica e di Scienze della Terra, Università di Messina, [5]MATIS IMM CNR e Dipartimento di Fisica, Università degli Studi di Catania

14.00-15.00 **SESSIONE POSTER: MS, ALI, CHEM, TOX, ELETTRO, FORE**

Sessione Parallela: **Alimenti e Nutraceutici - *Sala "Naxos Alcantara"***

Chairman: ***Ilario Losito***

15.00 – 15.30 **KN12** *THE USE OF COMPHENSIVE 2D LIQUID CHROMATOGRAPHY IN FOOD ANALYSIS*

P. Dugo[1,2,3], F. Cacciola[4], P. Donato[4], L. Mondello[1,2,3]

[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, [2]Chromaleont S.r.l., Messina; [3]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, [4]Dipartimento di Scienze Biomediche, Odontoiatriche e delle Immagini Morfologiche e Funzionali, Università degli Studi di Messina

15.30 – 15.50 **ALI-1** *HEAVY METAL SORPTION BY WATER KEFIR IN DIFFERENT CONDITIONS*

M. Cantamessa, M. Ginepro, V. Turone, G. Volpi, V. Zelano

Dipartimento di Chimica, Università degli Studi di Torino

15.50 – 16.10 **ALI-2** *INVESTIGATION BY RESPONSE SURFACE METHODOLOGY OF EXTRACTION OF CURCUMINOIDS FROM TURMERIC WITH ETHYL LACTATE AND MIXTURES OF BIOCOMPATIBLE SOLVENTS*

A.A. D'Archivio[1], M. A. Maggi[2], F. Ruggieri[1]

[1]Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila, Coppito, L'Aquila, Italy; [2]Hortus Novus, L'Aquila, Italy

16.10 – 16.30 **ALI-3** *ELECTRONIC TONGUE AND ELECTRONIC EYE FOR MONITORING MATURATION LEVEL OF GRAPES*

L. Pigani[1], G. Vasile Simone[1], G. Foca[2], A. Ulrici[2], F. Masino[2], R. Seeber[1]

[1]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia, Modena; [2]Dipartimento di Scienze della Vita, Università di Modena e Reggio Emilia, Padiglione Besta, Reggio Emilia

16.30 – 16.50 **Coffee Break**

16.50 – 17.10 **ALI-4** *DETERMINATION OF 7 TETRACYCLINES IN MILK AND EGGS BASED ON CONVENTIONAL HPLC/DAD USING A COLUMN PACKED WITH CORE-SHELL PARTICLES*

S. Summa[1], A. Armentano[1], S. Lo Magro[1], D. Centonze[2], M. Muscarella[1]

[1] Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata, Foggia; [2]Dipartimento di Scienze Agrarie, degli Alimenti e dell'Ambiente e CSRA, Università degli studi di Foggia

17.10 – 17.30 **ALI-5** *QUALITY ASSESSMENT AND AUTHENTICITY OF ITALIAN AND SERBIAN WINES*

P. Fermo[1], G. Giannelli[1], A. Mangone[2], Ž. Tešic[3]

[1]Dipartimento di Chimica, Università degli Studi di Milano; [2]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro; [3]University of Belgrade (Serbia), Faculty of Chemistry

Sessione Parallela: **Bioanalitica 3 + Sensori 3 - *Sala "Jonia"***

Chairman: ***Maria Careri***

15.30 – 15.50 **BIO-12** *PROTEOMIC STUDY OF INDONESIAN WILD SILK COCOON OF CRICULA TRIFENESTRATA AND BOMBYX MORI*

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

Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza"

15.50 – 16.10 **BIO-13** *A BIOANALYTICAL MEPS-UHPLC-PDA METHOD FOR THE SIMULTANEOUS DETERMINATION OF LINEZOLID AND CIPROFLOXACIN IN HUMAN PLASMA OF HOSPITAL ACQUIRED PNEUMONIA PATIENTS*

V. Ferrone[1], L. Di Marco[1], S. Genovese[1], R. Cotellese[2], M. Carlucci[2], P.Raimondi[2], G. Carlucci[1]

[1]Dipartimento di Farmacia, [2]Dipartimento di Scienze Mediche Orali e Biotecnologiche - Università degli Studi "*G. d'Annunzio*" Chieti-Pescara, Chieti

16.10-16.30 **BIO-14** *NEW ANALYTICAL SOLUTIONS FOR PHARMACEUTICAL NANO/BIOTECHNOLOGY*

B. Roda[1,2], A. Zattoni[1,2], V. Marassi[1], S. Casolari[1], P. Reschiglian[1,2]

[1]Department of Chemistry, University of Bologna, Bologna; [2] byFlow srl, Bologna, Italy

16.30 – 16.50 Coffee Break

16.50 – 17.10 **SENSO-12** *SELF-STANDING COATINGS BASED ON POLY(2-HYDROXYETHYL-METHACRYLATE) FOR AMPEROMETRIC SENSING*

C. Zanardi[1], S. Riso[1], M. Degli Esposti[2], P. Fabbri[2], R. Seeber[1]

[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Modena, Italia; [2] Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna

17.10 – 17.30 **SENSO-13** *CHARACTERIZATION OF NANOMATERIALS USING A DYNAMIC SURFACE TENSION DETECTOR (DSTD) AND DYNAMIC LIGHT SCATTERING*

M. Marongiu**,** V. Della Porta, B. Campanella, E. Bramanti

Istituto di Chimica dei Composti Organo Metallici, ICCOM-CNR Pisa

17.30 – 17.50 **SENSO-14** *A LOW COST CARBON BLACK MODIFIED SENSOR TO DETECT FREE CHLORINE IN WATER SAMPLES*

M. Tomei[1], D. Neagu[2], F. Arduini[1], D. Moscone[1]

[1]Dipartimento di Scienze e Tecnologie Chimiche, Università degli studi di Roma "Tor Vergata", Roma; [2]Tecnosens S.r.l, Via della Ricerca Scientifica, snc, Roma

17.50 – 18.10 **SENSO-15** *DETECTION OF ANTI-TISSUE TRANSGLUTAMINASE BY NANOELECTRODE ENSEMBLE BIOSENSORS FOR CELIAC DISEASE DIAGNOSTICS*

P. Ugo, H. H. Baye, S. Longo

Università Ca' Foscari Venezia -Department of Molecular Sciences and Nanosystems, Mestre, Venezia (Italy)

18.10 – 18.30 **SENSO-16** *EXPLOITING MULTICOLOR LUCIFERASES FOR SMARTPHONE-BASED BIOLUMINESCENCE CELL BIOSENSORS*

L. Cevenini[1], M.M. Calabretta[1], A. Lopreside[1], G. Tarantino[1], E. Michelini[1,2], A. Roda[1,2].

[1]Department of Chemistry "G. Ciamician", University of Bologna, Italy; [2]INBB, Istituto Nazionale di Biostrutture e Biosistemi, Roma, Italy

Sessione Parallela: **Chimica Forense + Tossicologia - *Sala "Etna"***

Chairman: ***Marco Vincenti***

15.00 – 15.30 **KN13** *PERMEATION OF METAL NANOPARTICLES THROUGH HUMAN SKIN, ORAL MUCOSA AND MENINGEAL MEMBRANES*

G. Adami

Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste

15.30 – 15.50 **FORE-1** *DETERMINATION OF OVER 60 DRUGS OF ABUSE IN HAIR BY PLE-DLLME EXTRACTION AND LC-HRMS ANALYSIS*

C. Montesano[1], G. Vannutelli[1], F. Vincenti[1], A. Gregori[2], L. Ripani[2], D. Compagnone[3], M. Sergi[3], R. Curini[1]

[1]Department of Chemistry, Sapienza University of Rome; [2]Department of Scientific Investigation (RIS-ROMA), Carabinieri, Roma; [3]Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo

15.50 – 16.10 **FORE-2** *TRACE DETECTION OF IMPROVISED EXPLOSIVES DEVICES (IED) FROM HUMAN HANDS: A PROMISING FORENSIC TOOL*

R. Risoluti[1], A. Gregori[2], L. Ripani[2], S. Materazzi[1]

[1] Department of Chemistry – "Sapienza" University of Rome, Italy; [2] Carabinieri RIS – Scientific Investigation Department, Rome, Italy

16.10 – 16.30 **FORE-3** *BROAD SCREENING AND IDENTIFICATION OF NOVEL PSYCHOACTIVE SUBSTANCES IN PLASMA BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY – HIGH RESOLUTION MASS SPECTROMETRY AND POST-RUN LIBRARY MATCHING*

C. Montesano[1], G. Vannutelli[1], A. Gregori[2], L. Ripani[2], D. Compagnone[3], M. Sergi[3], R. Curini[1]

[1]Department of Chemistry, Sapienza University of Rome; [2]Department of Scientific Investigation (RIS-ROMA), Carabinieri, Roma; [3]Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo

16.30 – 16.50 **Coffee Break**

Chairman: ***Gianpiero Adami***

16.50 – 17.10 **TOX-1** *MULTIVARIATE INVESTIGATION OF STEROIDOMIC PROFILES FOR CANCER DIAGNOSIS, PHYSIOLOGICAL ALTERATIONS RECOGNITION AND DOPING CONTROL*

E. Alladio[1,2], E. Amante[1,2], C. Bozzolino[1,2], E. Gerace[2], A. Salomone[2], M. Vincenti[1,2]

[1]Dipartimento di Chimica, Università di Torino; [2]Centro Regionale Antidoping "A. Bertinaria", Regione Gonzole 10/1, 10043 Orbassano, Torino, Italy

17.10 – 17.30 **TOX-2** *ALLOSTERIC DNA NANOSWITCHES FOR CONTROLLED RELEASE OF A MOLECULAR CARGO TRIGGERED BY BIOLOGICAL INPUTS*

M. Rossetti, S. Ranallo, A. Idili, G. Palleschi, A. Porchetta, F. Ricci

Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma "Tor Vergata"

17.30 – 17.50 **TOX-3** *PERCUTANEOUS ABSORPTION OF FLAME RETARDANTS*

M. Crosera[1], M. Venier[2], J. Guo[2], A. Phillips[3], H. Stapleton[3], F. Filon Larese[4], E. Baracchini[1], G. Adami[1]

[1]Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste; [2]School of Public and Environmental Affairs, Indiana University, Bloomington, Indiana; [3]Nicholas School of the Environment, Duke University, Durham, NC; [4]UCO Medicina del Lavoro, Dipartimento Universitario Clinico di Scienze Mediche, Chirurgiche e della Salute, Università di Trieste, Trieste

17.50 – 18.10 **TOX-4** *SAMPLING AND CHARACTERIZATION OF SUBMICRON AND ULTRAFINE PARTICLES: AN INTEGRATED APPROACH IN THE EXPOSURE ASSESSMENT DURING ALUMINIUM WELDING PROCESS*

E. Baracchini[1], A. Prodi[2], M. Crosera[1], P. Canton[3], F. Larese Filon[2] and G. Adami[1]

[1]Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste; [2]UCO Medicina del Lavoro, Dipartimento Universitario Clinico di Scienze Mediche Chirurgiche e della Salute, Università di Trieste; [3]Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Mestre

21.00 Cena Sociale (Atahotel Naxos Beach)

Giovedì 22 Settembre 2015

Sala "Naxos Alcantara"

09.00 – 09.45 Conferenza Plenaria **PL4** – Chairman: ***Aldo Roda***
Theodore Christopoulos (University of Patras, Greece)
NAKED-EYE SENSING OF NUCLEIC ACIDS

Sessione Parallela: **Beni Culturali 2 + Ambiente 3 -** ***Sala "Naxos Alcantara"***
Chairman: ***Claudio Minero***

10.10 – 10.30 **BC-8** *EVALUATION OF THE TOXICOLOGICAL IMPACT OF TEXTILE INDUSTRY USING A MULTI-CRITERIA RANKING OF TOXIC COMPOUNDS*
E. Gregoris[1,2], M. Roman[1,2], A. Gambaro[1,2], C. Barbante[1,2]
[1]Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari di Venezia; [2]Istituto per la Dinamica dei Processi Ambientali, Consiglio Nazionale delle Ricerche (IDPA-CNR)

10.30 – 10.50 **AMB-13** *PHOTOTRANSFORMATION OF PYRIDINIUM-BASED IONIC LIQUIDS IN WATER.*
P. Calza[1], D. Vione[1], D. Fabbri[1], G. Noè[1], C. Medana[2], C. Minero[1].
[1]Dipartimento di Chimica, Università di Torino; [2]Dipartimento di Biotecnologie Molecolari e Scienze per la salute, Università di Torino

10.50 – 11.10 **AMB-14** *BIODEGRADATION OF ANTHRACENE BY CHITOSAN MACROPARTICLES IMMOBILIZED LACCASE*
A. Apriceno, A. M. Girelli
Dipartimento di Chimica, Università La Sapienza, Roma

11.10 – 11.30 **Coffee Break**

11.30 – 11.50 **AMB-15** *COMPETITIVE ADSORPTION OF VOCs FROM AQUEOUS SOLUTIONS ON HYDROPHOBIC ZEOLITES*
E. Sarti[1], L. Pasti[1], A. Cavazzini[1], A. Martucci[2], E. Rodeghero[2], R. Bagatin[3]
[1]Department of Chemical and Pharmaceutical Sciences, University of Ferrara; [2] Department of Physics and Earth Sciences, University of Ferrara (Italy); [3] Research Center for Non-Conventional Energy, Istituto Eni Donegani Environmental Technologies, San Donato Milanese (MI, Italy)

Chairman: ***Danila Moscone***

12.00 – 12.20 **SENSO-17** *APPLICATION OF AN ELIME ASSAY FOR THE DETECTION OF SALMONELLA IN VEGETABLES*
L. Fabiani[1], G. Volpe[1], E. Delibato[2], E. Pucci[2], S. Piermarini[1], G. Palleschi[1]
[1]Department of Chemical Science and Technologies, University of Tor Vergata, Roma; [2] Department of Veterinary Public Health and Food Safety, Istituto Superiore di Sanità, Rome

12.20 – 12.40 **SENSO-18** *A DNA NANODEVICE THAT LOADS AND RELEASES A CARGO WITH HEMOGLOBIN-LIKE COOPERATIVITY*
D. Mariottini[1], A. Idili[1], A. Vallée-Bélisle[3], K. W. Plaxco[2], F. Ricci[1].
[1]Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Roma; [2]Department of Chemistry and Biochemistry, University of California, Santa Barbara; [3]Département de Chimie, Universite´ de Montréal, Laboratory of Biosensors and Nanomachines, Québec, Canada

Sessione Parallela: **Chemiometria e qualità del dato + Sensori 4 - *Sala "Jonia"***

Chairman: ***Riccardo Leardi***

10.00 – 10.30 **KN14** *CALIBRATION TRANSFER BETWEEN NEAR-INFRARED SPECTROMETERS: A COMPREHENSIVE OVERVIEW*

R. Vitale

Grupo de Ingeniería Estadística Multivariante, Departamento de Estadística e Investigación Operativa Aplicadas y Calidad, Universitat Politècnica de València, Valencia, Spain

10.30 – 10.50 **CHEM-1** *BEWARE OF UNRELIABLE Q^2! A COMPARATIVE STUDY OF REGRESSION METRICS FOR PREDICTIVITY ASSESSMENT OF QSAR MODELS*

R. Todeschini, D. Ballabio and F. Grisoni

Milano Chemometrics and QSAR Research Group, Department of Earth and Environmental Sciences, University of Milano-Bicocca, P.za della Scienza, 1 – 20126 Milan (Italy)

10.50 – 11.10 **CHEM-2** *COLOURGRAMS-GUI: A GRAPHICAL USER INTERFACE FOR EXTRACTING USEFUL INFORMATION FROM RGB IMAGES*

R. Calvini, G. Orlandi, G. Foca, A. Ulrici

Dipartimento di Scienze della Vita, Università di Modena e Reggio Emilia, Reggio Emilia

11.10 – 11.30 **Coffee Break**

11.30 – 11.50 **CHEM-3** *STRATEGIES FOR NON-LINEAR MODELING*

F. Marini

Dipartimento di Chimica, Università di Roma "La Sapienza", Roma

11.50 – 12.10 **CHEM-4** *EVALUATION OF DIRECT ALCOHOL BIOMARKERS USING MULTIVARIATE AND LIKELIHOOD RATIO APPROACHES TO IDENTIFY CHRONIC ABUSERS FOR FORENSIC PURPOSES*

E. Alladio[1,2], A. Martyna[3,4], A. Salomone[2], V. Pirro[5], M. Vincenti[1,2], G. Zadora[4,6]

[1]Dipartimento di Chimica, Università di Torino, Italy; [2]Centro Regionale Antidoping e di Tossicologia "A. Bertinaria", Orbassano, Torino, Italy; [3]Faculty of Chemistry, Jagiellonian University, Krakow, Poland; [4]Institute of Forensic Research, Krakow, Poland; [5]Department of Chemistry, Purdue University, Indiana, USA;[6]Department of Analytical Chemistry, Chemometric Research Group, The University of Silesia, Katowice, Poland.

Sala "Naxos Alcantara"

12.45 **Chiusura del Congresso**

Plenary Lectures

DEVELOPMENT OF ANALYTICAL DEVICES AND PROCEDURES CONSISTENT WITH GREEN CHEMISTRY

J. Pawliszyn
University of Waterloo, Department of Chemistry, 200 University Ave. W., Waterloo, ON N2L 3G1, Canada

The talk will cover devices developed in my laboratories facilitating "green" analytical procedures. In particular focus will be placed on sample preparation techniques such as SPME, Thin Film Microextraction (TFME), Needle Trap (NT), Membrane Extraction with Sorbent Interface (MESI) and Supercritical Fluid Extraction (SFE). Appropriate deployment of these sampling/sample preparation tools facilitate on-site deployment and provide more information about the investigated system, the features which will be highlighted. For example, by combining SPME and NTD extraction allows for the differentiation of free and particulate bound compounds in a gaseous sample matrix. Samples may contain both solid and liquid aerosols in addition to freely dissolved analytes. Where analytes of interest preferentially bind to the aerosols, the free concentration may be significantly lower than expected. The NTDs trap both gaseous chemical compounds as well as particulate matter present in the sample. SPME samples only the freely dissolved analytes. Thus SPME and NTD together can differentiate these and provide a more complete characterization of aerosol samples. Using high temperature SFE/SPME or NT desorption facilitates characterization of adsorbed organics. To increase sensitivity of the SPME measurement the DVB or carboxen particle loaded tin film membranes were used as the extraction phase. This technique is based on a similar principle as the fiber technique with additional advantage of higher surface to volume ratio facilitating much higher extraction rates and higher sensitivities because of high volume of the extraction phase. More specifically, the development of the thin film sampler involved cutting a section of thin-film into a specific size and shape, and mounting it onto a stainless steel wire (the handle). This technique was used as rapid spot or TWA sampling of environmental samples. For rapid water sampling, an electric drill was used to rotate the thin-film to get higher sampling rate.

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DIRECT ELECTRON TRANSFER BETWEEN SUGAR OXIDISING ENZYMES AND ELECTRODES AS BASIS FOR 3RD GENERATION BIOSENSORS/BIOANODES

Lo Gorton
Lund University, SE-221 00 Lund, Sweden

A number of new sugar oxidising redox enzymes and variants thereof, *viz*. pyranose dehydrogenase (PDH) [1], pyranose oxidase (P2O) [2], and cellobiose dehydrogenase (CDH) [3,4] have recently been electrochemically characterised for use in biosensors and biofuel cell anodes [1,5]. These redox enzymes come from different basidiomycetes or ascomycetes and are all glycosylated and contain strongly bound FAD in the active site. CDH additionally also contains a cytochrome *b*. Electron transfer between these enzymes and electrodes can be obtained through different mediated approaches using 2 e^- H^+ acceptors or 1 e^- acceptors. Additionally due to its cytochrome *b* domain CDH shows very facile direct electron transfer (DET) characteristics with electrodes making 3rd bioelectrodes possible [3,4]. CDH similarly to glucose oxidase oxidises the sugar on the C1 carbon making it anomeric specific and selective for the ß-form. Depending on the origin class I CDHs selectively oxidise lactose and cellodextrins, whereas class II CDH may also oxidise glucose [3,4]. In contrast PDH and P2O oxidise the sugar on the C2 or C3 carbon (or on both) making them anomeric insensitive. Both PDH and P2O are highly unselective and PDH even oxidises sucrose with a high turn-over rate [1]. Additionally especially for PDH there is a possibility that the oxidation product is also a substrate and one sugar molecule can be oxidised at least twice and is thus a very valuable redox enzyme for biofuel cell studies [1]. To improve DET these enzymes can be deglycosylated. However, deglycosylation also increases the risk that non-covalently bound FAD may come out of the active site. As PDH has a covalently bound FAD, deglycosylated PDH remains fully active and electrodes modified with this shows much increased current densities [1].

References

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[2] O. Spadiut, D. Brugger, V. Coman, D. Haltrich, L. Gorton, Electroanalysis, 22 (2010) 813-820.
[3] R. Ludwig, W. Harreither, F. Tasca, L. Gorton, ChemPhysChem, 11 (2010) 2674-2697.
[4] R. Ludwig, R. Ortiz, C. Schulz, W. Harreither, C. Sygmund, L. Gorton, Anal. Bioanal. Chem., 405 (2013) 3637–3658

[5] M. Falk, M. Alcalde, P. N. Bartlett, A. L. De Lacey, L. Gorton, C. Gutierrez-Sanchez, R. Haddad, J. Kilburn, D. Leech, R. Ludwig, E. Magner, D. M. Mate, P. Ó Conghaile, R. Ortiz, M. Pita, S. Pöller, T. Ruzgas, U. Salaj-Kosla, W. Schuhmann, F. Sebelius, M. Shao, L. Stoica, C. Sygmund, J. Tilly, M. D. Toscano, J. Vivekananthan, E. Wright, S. Shleev, Plos One, 9 (2014) e109104.

LIPIDOMICS - FROM QUANTIFICATION TO CLINICAL APPLICATION

G. Liebisch
Institute of Clinical Chemistry and Laboratory Medicine, University of Regensburg, Germany

The molecular composition of lipids has great influence on biological functions by modulation of membrane fluidity and curvature. This affects signaling processes as well as activity of membrane bound enzymes including those linked to lipoproteins.
Electrospray tandem mass spectrometry (ESI-MS/MS) offers an excellent platform to quantify lipid species with high sample throughput. Major glycerophospholipid and sphingolipid classes are accessible by direct flow injection of crude lipid extracts. Whereas low abundant or isobaric species require frequently liquid chromatographic separation coupled to tandem mass spectrometry (LC-MS/MS). These methods provide insight into the dynamics of the lipid species metabolism and transport processes by administration of stable isotope labeled precursors or lipid species. For example major pathways of the glycerophospholipid metabolism may be profiled using D_9-choline, D_4-ethanolamine and $^{13}C_3$-serine.
Lipid species quantitation is applicable for biomarker search in large clinical studies as well as basic research in a variety of sample materials including plasma, lipoprotein fractions, cells and tissues. Lipid species are already applied as diagnostic marker of monogenetic diseases e.g. lysosomal disorders and several studies implicate their potential as biomarker e.g. for cardiovascular risk or cancer.
Taken together, mass spectrometry offers a powerful tool box to discover novel lipid biomarker in the blood compartment and to unravel mechanisms underlying the regulation of the lipid metabolism.

NAKED-EYE SENSING OF NUCLEIC ACIDS

T. Christopoulos
Department of Chemistry, University of Patras, Rion-Patras, Greece 26504

This presentation focuses on the architecture and functional aspects of disposable, dipstick-type DNA biosensors that enable visual detection of single nucleotide polymorphisms. Their advantages are: simplicity, low cost, portability, no need for specialized equipment, as well as, elimination of multiple pipetting, incubation and washing steps. For genotyping, the interrogated sequence is subjected to exponential amplification and allele-discrimination reactions. The product is applied to the sample area of the biosensor, which is then immersed in the appropriate buffer. Detection is accomplished by using gold nanoparticles, carbon nanoparticles, colored latex particles or quantum dots that are functionalized either with oligonucleotide or antibody. The appearance of a characteristic colored line or spot at the test zone indicates the presence of the ‘normal’ or ‘mutant’ allele in the sample. Multialle visual genotyping by a single biosensor has also been achieved. The biosensors have been applied successfully to both molecular diagnosis of disease and food authenticity testing.

Premio Giovane Ricercatore

DETERMINATION OF GASEOUS SPECIES TRANSFORMATION RATE IN FLOW REACTORS: SOME CASE-STUDIES OF ENVIRONMENTAL CONCERN

M. Minella, C. Minero
Dipartimento di Chimica, Università degli Studi di Torino, Via P. Giuria, 5 – 10125 Torino

The accurate determination of gaseous species has a widespread importance in both technological and pure scientific contexts. These measurements are routinely carried out for emissions in atmosphere, the control of the catalytic converters of vehicles, for testing the depollution ability of the filters at the end of the chimneys, or for the determination of the rate of gaseous reactants transformation. The accurate determination of the transformation rate in the gas phase finds a direct application in the study of reactions of atmospheric concern, and for the determination of the working mechanism of catalysts for solid-gas transformations.
Usually analysts are primarily focused on the detector and on its performances, while less attention is placed on the type of the reactors. Contrariwise, this is a peculiar point because it affects directly the way data are interpreted.[1] The determination of the rate of transformation can be carried out both in *bulk reactors*, in which the concentration of the desired species is monitored as a function of time, and in *flow reactors*, in which the analyte is detected at the exit of the reactor continuously fed with reactants. The evaluation of $[A_i]$ needs proper analytical techniques and it is well known standard (static) analytical problem. The standard (dynamic) analytical problem involved in the evaluation of a fast $d[A_i]/dt$ in batch reactors needs only short integration time of the detector. The evaluation of a dynamic property is a challenging (dynamic) analytical problem, that requires the correct choice of the proper fast technique and possibly of defined molecular probes, but often can be bypassed by the proper configuration of the reactor (any probe molecules with standard technique). This could be a basic contribution of analytical chemistry as multisciplinary science to industrial, environmental and standardization issues.
Three case studies of environmental concern in which flow reactors have been tested will be shown: *i*) the measure of the NO/NOx abatement rate on irradiated photocatalytic specimens; *ii*) the determination of the O_3 abatement rate on innovative catalysts and *iii*) the study of the NO photolysis under Vacuum UV irradiation. A comparison between the bulk and the in-flow measurements of gaseous species will be presented with the aim to underline the merits (many) and the defects (few) of the use of flow reactors vs. bulk systems.

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Keynotes

COMPOSITION, SOURCES AND MITIGATION STRATEGIES FOR PM10 AND PM2.5 IN SOUTH EUROPE. MAIN RESULTS FROM THE LIFE+ AIRUSE PROJECT.

R. Udisti[1], M. Chiari[2], M. Giannoni[2,3], F. Lucarelli[3], S. Nava[2], G. Calzolai[3], S. Becagli[1], R. Traversi[1], X. Querol[4], F. Amato[4], V. Gianelle[5], C. Colombi[5], C. Alves[6], D. Custódio[6], K. Eleftheriadis[7], E. Diapouli[7], R. Harrison[8], C. Holman[8]

[1] Dip. Chimica, Univ. Firenze, via della Lastruccia 3, 50019 Sesto F.no (FI).
[2] INFN, Firenze, via G. Sansone 1, 50019 Sesto F.no (FI).
[3] Dip.Fisica e Astr., Univ. Firenze, via G. Sansone 1, 50019 Sesto F.no (FI).
[4]Inst. Environ. Assess.-Water Res.(IDAEA-CSIC), 08034 Barcelona, Spain.
[5]Arpa Lombardia, Via Rosellini 17, I-20124 Milano, Italy
[6]Environment Dept., Aveiro Univ., 3810-193 Aveiro, Portugal
[7]Env. Radio. Lab, NCSR Demokritos, 15341 Ag. Paraskevi, Attiki, Greece
[8]Geogr., Earth & Env. Sci., Birmingham Univ., Birmingham B15 2TT, UK

The AIRUSE Project (Testing and development of air quality mitigation measures in Southern Europe), funded by the European Program LIFE+, was aiming to identify the PM sources in South Europe urban areas and to quantify their contributions in the different anthropic environments. Similitudes and differences were evaluated and discussed in order to test and propose mitigation strategies, and to address suitable air-quality policies.
In the period January 2013 – January 2014, daily PM10 and PM2.5 samples were contemporaneously collected in 5 European urban cities: Barcelona, Florence, Milan, Porto and Athene. Filters were analyzed by PIXE (elemental composition), ICP-MS (main and trace metals), Thermo-Optical Analyzer (EC and OC fractions), IC (inorganic anions and cations and selected organic anions). Some samples were also analyzed for levoglucosan, a specific biomass burning marker. Shorter samplings were carried out with a streaker sampler, in order to collect the aerosol at higher resolution (1-hour). The obtained data set was processed by multivariate statistical analysis (PMF – Positive Matrix Factorization), in order to perform the source apportionment. The main sources were traffic, domestic eating (especially biomass burning for Porto, Milan and Florence) and secondary aerosol (by photochemical reactions). Natural sources, such as dust (especially Saharan dust events) and sea spray played a significant role in the PM10 budget, too. The AIRUSE project included specific tasks, such as the evaluation of the emission factors for pellet and wood stoves, and the estimation of the traffic dust lifting contribute. The effect of mitigation strategies (road washing with different chemical agents) were also tested. In this presentation, we report the main AIRUSE results.

RECENT TRENDS IN ANALYSIS OF BIOACTIVE PEPTIDES IN FOOD MATRICES

A.L. Capriotti
Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", Piazzale Aldo Moro, 5 – 00185 Roma

Food-derived constituents represent important sources of several classes of bioactive compounds. Among them peptides have gained great attention in the last two decades thanks to the scientific evidence of their beneficial effects on health in addition to their established nutritional value.
Several functionalities for bioactive peptides have been described, including antioxidative, antihypertensive, anti-inflammatory, immunomodulatory, and antimicrobial activity. They are now considered as novel and potential dietary ingredients to promote human health, though in some cases they may also have detrimental effects on health. Bioactive peptides can be naturally occurring, produced in vitro by enzymatic hydrolysis, and formed in vivo during gastrointestinal digestion of proteins.
This keynote provides an overview of my research activity focusing mainly on the major developments in the field of peptidomic sciences, telling some success stories as well as challenges that are currently being faced.
The keynote highlights the prospects of bioinformatics and a proposed integrated approach for enhancing the production of existing and
new bioactive peptides from sustainable food protein sources, followed by a critical evaluation of the major challenges that may impact prospective commercialization of food bioactive peptides for use in human health promotion. Examples of promising applications of these peptides in food, nutraceuticals and cosmeceuticals will be also discussed with an insight to the future research needs.

ALLOSTERIC CONTROLLED DNA-BASED NANODEVICES FOR BIOSENSING APPLICATIONS

A. Idili, A. Amodio, M. Rossetti, G. Palleschi, A.V. Belisle, K. Plaxco, F. Ricci, A. Porchetta[1]
[1]Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Tor Vergata, Roma, Via della Ricerca Scientifica, 1, 00133, Italia
[2]Department of Chemistry and Biochemistry, University of California Santa Barbara, CA 93106, USA.
[3] Departement de Chimie, Université de Montréal, 6128, Quebec (Canada).

One intrinsic limitation of biomolecular recognition event is represented by the fixed dynamic range of target concentration that can be measured using a biomolecule as a receptor. Specifically, the physics of single-site binding produces a hyperbolic dose−response curve for which the useful dynamic range spans a fixed change in target concentration. This fixed dynamic range complicates (or even precludes) the use of biosensors in many applications.
Allostery, also defined "the second secret of life", is one of the most widely used mechanisms by which nature overcomes this limitation. The ubiquity with which nature employs this mechanism suggests that engineering allostery into synthetic systems could improve the functionality of biomolecules for biosensing purpose.
Motivated by the above arguments, we adapted naturally occurring allosteric control on DNA-based nanoswitches to finely regulate their dynamic range of target detection. We demonstrated that using allostery is possible to tune, extend and narrow the fixed dynamic range. More specifically, we developed allosterically regulated DNA-based nanodevices that can detect different targets such as oligonucleotides[1], small molecules[2], heavy metals ions[3] and transcription factors[4] in a controlled fashion. By taking advantage of this strategy we also demonstrated the ability to re-engineer DNA-based switches that can be activated and inhibited in presence of specific allosteric effectors[6].

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SPECIATION IN SOLUTION: IS IT WORTH DOING IT?

G. Arena
Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale A. Doria, 6 – 95125 Catania

When talking of speciation our mind often goes back to the Minamata Bay disaster or to the more recent poisoning outbreak in several parts of the world due to the same chemical [1]. These simple though baleful examples clearly show that it is not so much the total concentration of the element but the specific molecular form/species of the element that is responsible for its harmful or beneficial effect. For a long time now it has been recognized that it is not incorrect to ascribe to analytical chemistry a position of primary importance, since only through chemical analysis can matter in its variety of forms be dealt with intelligently. Yet, it has also been emphasized that "*The determination of total trace element concentrations is a first step toward complete characterization of ...*" and that "*The crude use of total element criteria will become unnecessary as appropriate research employing techniques for speciation is performed*" [2].
The knowledge and/or the determination of the species present in a system is the first step for the speciation of a naturally occurring compartment. The determination of the thermodynamic parameters for each species comes next. Einstein considered thermodynamics was the only physical theory that was so well based on experiment that it would never be overthrown [3]; despite its solidity, thermodynamic characterization may be insufficient since the various species (often several thousands) may not be under true equilibrium conditions. Though simple techniques (e.g. potentiometry, UV-vis and NMR, calorimetry, etc) can be employed, yet extending experimental results to real matrices may not be an easy task owing to the difference between the experimental conditions (e.g. temperature and concentrations) the parameters are obtained at and the actual matrix conditions.
A few examples covering different chemistry fields will be presented showing that perhaps determining the species distribution is not just an exercise but is essential for a correct interpretation of the chemistry going on in real matrices [4-7].

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UTILIZATION OF SPME-LC-MS PLATFORM FOR PROFILING OF METABOLIC CHANGES IN ORGANS PRIOR TRANSPLANTATION

B. Bojko[1,2], I. Stryjak[1], K. Gorynski[1], G. A. Gomez-Rios[2], E. Cudjoe[2], and J. Pawliszyn[2]
[1] Department of Pharmacodynamic and Molecular Pharmacology, Faculty of Pharmacy, Nicolaus Copernicus University, Dr. A. Jurasza 2, 85-089 Bydgoszcz, Poland
[2] Department of Chemistry, University of Waterloo, 200 University Ave. W., Waterloo, ON, N2L 3G1 Canada

Transplantation is life-saving procedure. However, despite of rapidly developing technologies there is still dramatic restriction of tools available for efficient evaluation of organs quality and function. The effective selection of grafts would enable to decrease number of rejections and increase the pool of high quality organs available for transplantation without waste of those which carry potential risk of rejection based on the visual or basic-parameter inspection.
Because of the simplicity of in vivo solid phase microextraction method, which combines sample preparation, metabolism quenching and extraction as well as eliminates sample collection we proposed introduction of the approach to monitoring graft function at different stages of the medical procedure related to organ transplantation. To ensure the best analytical performance of the method, various aspects of the protocol were studied and optimized including selection of coating length, analyte coverage, transportation and storage conditions with particular attention paid to stability of the extracted compounds and convenience of the approach for clinical setup. The proposed approach was used for monitoring of metabolic profile of kidneys, lung and liver in animal models during.
The obtained results showed that in situ and in vivo SPME coupled to UPLC-HRMS platform could be successfully used for timecourse metabolomics studies of grafts by eliminating need for biopsy collection thus preventing organ damage. In the same time gained information reflects well status of the organ and selected compounds, after proper validation, could be used as biomarkers of graft condition enabling physician making more confident decision on its transplantation.

SURFACE XPS STUDY OF ION EXCHANGE IN ERIONITE

M. Fantauzzi[1], A. Pacella[2]
[1]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, s.s. 554 bivio per Sestu – 09042 Monserrato (CA)
[2]Dipartimento di Scienze della Terra, Sapienza Università Roma, Piazzale Aldo Moro – 00185 Roma

Erionite is a natural occurring fibrous zeolite with general formula $(Na_2,K_2,Ca,Mg)_{4.5}Al_9Si_{27}O_{72} \bullet 27H_2O$. It is known to be carcinogenic, belonging to Group I, Human Carcinogens, according to IARC classification [1]. Due to its characteristics it may act as an ion exchanger and its toxicity has been partly ascribed to its ion-exchange properties and/or to the presence of surface-deposited Fe participating in Fenton chemistry.
In the present work, the results of a detailed surface characterization by X-ray photoelectron spectroscopy (XPS) of different erionite samples from USA are presented. The samples were analysed in the pristine state and after immersion in $FeCl_2$ solutions (concentration ranging between 100 and 1000 μM) [2] and in $FeCl_3$ solutions (concentration ranging between 250 and 1000 μM) to investigate the iron uptake by erionite.
The samples loaded with $FeCl_3$ were then immersed in an ascorbic acid solution for 1 and 24 hours (6 mM, T = 37°C) for evaluating the iron reduction, for monitoring the mobility of reduced Fe (II) and for detecting its possible incorporation as extra - framework cation through ion exchange.
XPS analyses showed that in $FeCl_2$ solutions, the amount of loaded Fe increased with the concentration of the solutions and, among the Fe 2p components, the higher was the $[FeCl_2]$ the more intense was the component ascribed to Fe (II). At the same time a dramatic decrease of sodium content was observed. In $FeCl_3$ solutions it was observed an iron enrichment and sodium depletion, as well. Following the contact with ascorbic acid, Fe (II) was detectable only for the sample loaded with the 250 μM $FeCl_3$ solution and its concentration at the mineral surface increased with the immersion time. In the sample loaded with 1000 μM $FeCl_3$ only Fe (III) was detected after contact with the ascorbic acid. This result evidences that the higher degree of Fe (III) polymerization in the most concentrated solution promotes the precipitation of Fe (III) oxides and oxy-hydroxides at the fibre surface characterised by increased iron nuclearity that inhibits the interaction between the iron centres and ascorbic acid.

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A SIMPLE SMARTPHONE BIOSENSOR BASED ON SILICA FUNCTIONALIZED NANOPARTICLES DOPED WITH NEW THERMOCHEMILUMINESCENT ACRIDINE-1,2-DIOXETANE DERIVATIVES AS UNIVERSAL REAGENT-LESS LABEL FOR BIOASSAYS

M. Mirasoli, L.A. Andronico, D. Calabria, A. Quintavalla, M. Lombardo, C. Trombini, A. Roda
Department of Chemistry ‘‘Giacomo Ciamician’’, Alma Mater Studiorum, University of Bologna, Via Selmi, 2 – 40126 Bologna

We recently demonstrated that thermochemiluminescence (TCL), i.e. the photon emission originating from the thermolysis of a suitable molecule which leads to a singlet excited state product, is a powerful tool for biosensors development [1]. TCL has the unique feature of allowing reagent-less detection, as only a thermal shock is required to trigger light emission from the TCL label, thus simplifying the microfluidic network with respect to chemiluminescence (CL)-based miniaturized biosensors.
We previously synthesized a library of new TCL acridine-1,2-dioxetane derivatives, characterized by emission triggering temperatures down to 80−100°C and yielding highly efficient emitters (fluorescence quantum yields in the range 0.1-0.5) [2]. To obtain signal amplification, organically modified silica nanoparticles (ORMOSIL NPs) doped with TCL molecules were prepared and functionalized with biotin to be used as detection reagents for binding assays. A quantitative non-competitive immunoassay for streptavidin was developed, with analytical performance similar to that obtained with horseradish peroxidase-based CL detection (LOD 3 µg/mL).
As previously demonstrated for CL detection [3], herein we describe a smartphone-based compact 3D-printed device, developed for TCL bioassays, comprising a mini dark box and a Li battery-powered mini-heater. A personalized App was developed for image processing and data transmission. The device was exploited to develop a competitive TCL immunoassay for the antiepileptic drug valproic acid, employing paper-based analytical format. The method presents a good precision and accuracy, with of LOD of 1 ng/mL. We thus demonstrate that, for biosensors development, the smartphone is not auxiliary but rather forms the core of the analytical platform.

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RECENT TRENDS IN THE EMPLOYMENT OF ELECTROCHEMICAL TECHNIQUES FOR THE CHARACTERIZATION OF CORROSION PRODUCTS OF ARCHAEOLOGICAL METALS

F. Di Turo[a], N. Montoya[b], J. Piquero-Cilla[b], C. De Vito[a], R. Antiochia[c], F. Mazzei[c], G. Favero[c], A. Doménech-Carbó[b]

[a] Department of Earth Sciences, Sapienza University of Rome, P.le Aldo Moro 5, Rome, Italy

[b] Departament de Química Analítica. Universitat de València. Dr. Moliner, 50, 46100 Burjassot (València) Spain.

[c] Department of Chemistry and Drug Technologies, Sapienza University of Rome, P.le Aldo Moro 5, Rome, Italy

Scientific examination of archaeological pieces and works of art is undoubtedly a necessary task for archaeometry, conservation and preservation/restoration sciences. Numerous methodologies have been extensively applied in the study of ancient metal artefacts, including Scanning Electron Microscopy (SEM-EDS), X-ray Diffraction (XRD), μ-Raman spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Laser Inductively Coupled Plasma (LA-ICP-AES) and other techniques. Although essentially focused on metal corrosion problems, electrochemistry was one of the early applied scientific methodologies, in both its analytical and conservative/restorative aspects. Over the last few decades, the scope of electrochemical methods' ability to interact with archaeometry, conservation and restoration has been significantly extended, by virtue of the application of new approaches—in particular, the voltammetry of microparticles (VMP) and electrochemical impedance spectroscopy (EIS).

The VMP, based on the record of voltammetric response of a solid micro- or nanosample mechanically transferred to the surface of an inert electrode immersed into an appropriate electrolyte, is particularly suitable for archaeometric analysis because of its high inherent sensitivity and ability to identify the corrosion products. On the other hand, EIS, already applied in studies of Cultural Heritage materials especially in evaluating coating treatments effectiveness, demonstrated also to be suitable for the evaluation of deterioration and patina's formation because it can provide not only quantitative data but refers to corrosion processes and alteration products too.

The characterization of the patina formed on archaeological metals can benefit from the employment of both traditional (stereomicroscopy (SM), scanning electron microscope (SEM) and X-ray diffraction (XRD)) and electrochemical techniques, where in particular, VMP can be applied to distinguish samples different for age or mint and complemented with EIS operating either in solution or using a gel polymer electrochemical cell suitable for surface mapping of deterioration products.

NEW FRONTIERS IN APPLICATION OF FTIR MICROSCOPY FOR THE CHARACTERIZATION OF CULTURAL HERITAGE MATERIALS

R. Mazzeo, S. Prati, G. Sciutto, I. Bonacini
Dipartimento di Chimica "G. Ciamician", Laboratorio diagnostico di microchimica e microscopia (M2ADL) per i beni culturali, Università di Bologna – Campus Ravenna, Via Guaccimanni 42, 48100, Ravenna (Italia)

An overview of recent advances in the application of Fourier Transform Infrared (FTIR) microscopy for the analysis of complex, multicomponent, and multilayer samples, such as those typically encountered in the field of heritage materials, will be presented.
FTIR spectroscopic methods are particularly useful since they allows identification and localization of both organic and inorganic (if IR active) compounds. New improvements have been possible thanks to the introduction of ad hoc sample preparation methods to obtain either thin or cross sections that allow both avoidance of contamination from organic embedding resin and improvement of the quality of the acquired spectra. Moreover, integrated use of spectra registered in the near-infrared (NIR) and mid-infrared (MIR) regions allows better comprehension of cross section composition. Data interpretation has been improved thanks to the development of chemometric methods for elaboration of hyperspectral data. A new and very promising field is the development of enhanced FTIR methods for detection of trace components in micro extracts. These systems, allowing detection of extractable organic compounds from about 0.1 mg of sample, will be extremely useful in the future for analysis of natural and synthetic colorants, varnishes extracted, for instance, from cotton swabs used during cleaning of paintings, and organic residues on archaeological remains.

NANOSTRUCTURED ELECTROCHEMCIAL BIOSENSING PLATFORMS FOR NUCLEIC ACID DETECTION

I. Palchetti
Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3,50019, Sesto Fiorentino (FI), Italy

Electrochemical genosensors have been intensively studied due to their potential for nucleic acid testing, as a result of their appropriate sensitivity, multiplexing capability, their simplicity to use, low cost, and small amount of sample required.
Electrochemical techniques, such as faradic impedance spectroscopy, chronoamperometry, and differential pulse voltammetry, have been used by our group, for the development and characterization of different format of genosensors. Basically, the DNA capture probes are immobilized on the electrode surfaces. Then, the target sequence is extracted from the sample, and hybridized with the specific capture probes.
The electrode surface nanostructuring offers suitable anchoring sites for the capture probes allowing optimal control over steric hindrance.
Recently, we have optimized a procedure to electrodepositate gold nanoclusters to define nanoscale immobilization domains, where a few DNA strands are immobilized at a time, thus limiting packing and consequently steric hindrance and electrostatic repulsion during the hybridization and labeling steps. Nanoarchitectures, rich in enzyme labels, have been then coupled in order to increase the overall sensitivity of the assay.
In a further approach, a label-free impedimetric genosensor has been developed, using a miniaturized, polymer-modified sensor. In particular, a polymer bearing an intact biotin moiety available for streptavidin binding has been used. As a result, the sensor surface has been nanostructured, thus increasing the capture probe immobilization efficiency in terms of orientation, loading and steric hindrance.
These examples are here discussed in details. Preliminary results on a photoelectrochemical assay based on AuNP modified TiO_2 electrodes will be also discussed.

NATIVE AND OXIDIZED FREE FATTY ACIDS IN MUSSELS INVESTIGATED BY LIQUID CHROMATOGRAPHY-ELECTROSPRAY IONIZATION-FOURIER TRANSFORM MASS SPECTROMETRY

I. Losito[1,2], L. Facchini[1], A. Valentini[1], T.R.I. Cataldi[1,2], F. Palmisano[1,2]

[1]Dipartimento di Chimica, [2]Centro di Ricerca Interdipartimentale SMART, Università degli Studi di Bari "Aldo Moro", Via E. Orabona, 4 – 70126 Bari

With an estimated amount of ca. 3 million tons per year mussels represent one of the most diffused aquaculture-based shellfish products worldwide [1]. Due to transportation and storage requirements, they are usually subjected to different low-temperature treatments (like refrigeration and glazing [2]), before being commercialized. Nonetheless, inappropriate procedures, like storage at room temperature, are not rare on the market and represent a potential threat for the safety and quality of this product. A recent study, based on the coupling between hydrophilic interaction liquid chromatography (HILIC) and electrospray ionization Fourier-transform tandem mass spectrometry (ESI-FT-MS/MS), has emphasized a relationship between thermal treatments and variations in the lipid component of mussels [3]. In particular, an increase in the amount of *Lyso*-phospholipids (LPL) has been observed upon treatments at low or room temperature and explained with the occurrence of phospholipid hydrolysis catalyzed by endogenous phospholipases. To confirm this assumption a systematic investigation on mussel free fatty acids (FFA) has been undertaken and will be the object of the present communication. FFA, extracted from mussel samples and separated from phospholipids through solid phase extraction (SPE) on a silica stationary phase, were analyzed using a core-shell reverse phase column coupled to a high resolution/accuracy FT orbital-trap mass spectrometer, enabling also tandem mass spectrometry acquisitions based on high energy collision induced dissociation (HCD). As a result, 257 different FFA (with up to 222 in a single lipid extract), including species bearing oxygenated moieties (i.e., hydroxylic, epoxidic and carbonylic groups), were recognized. Interestingly, the processing of data based on Principal Component Analysis suggested the possibility of using specific FFA as molecular markers of thermal stresses suffered by mussels.

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THE USE OF COMPHENSIVE 2D LIQUID CHROMATOGRAPHY IN FOOD ANALYSIS

P. Dugo[1,2,3], F. Cacciola[4], P. Donato[4], L. Mondello[1,2,3]
[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Polo Annunziata, Viale Annunziata - 98168 Messina
[2]Chromaleont S.r.l., Viale Boccetta, 70 - 98122 Messina
[3]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, via Álvaro del Portillo 21, 00128 - Roma
[4]Dipartimento di Scienze Biomediche, Odontoiatriche e delle Immagini Morfologiche e Funzionali, Università degli Studi di Messina, Viale Consolare Valeria - 98165 Messina

One-dimensional chromatography is the most widely applied technique to the analysis of real-world samples in various fields. However, more powerful analytical techniques e.g. comprehensive two-dimensional liquid chromatography (LC×LC) are necessary whenever the complexity of the sample overwhelms the separation capability afforded by a single separation system. LC×LC techniques involving complementary separation modes combined in the two-dimensions, has been investigated with an ever increasing interest in the past two decades.
For small molecules, e.g. polyphenols occurring in food products, one of the most used LC×LC set-up is the reversed phase×reversed phase approach (RP-LC×RP-LC), where the orthogonality can be augmented using different stationary phases and/or different mobile phases. More recently, HILIC×RP-LC has gained a great attention due to clear advantages offered, such as the use of complementary separation mechanisms and compatibility of mobile phases employed.
In this contribution, some applications involving the use of the LC×LC technique are illustrated. Also, some aspects regarding the use of dedicated software programs for data handling in LC×LC are emphasized.

PERMEATION OF METAL NANOPARTICLES THROUGH HUMAN SKIN, ORAL MUCOSA AND MENINGEAL MEMBRANES

G. Adami
Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via L. Giorgieri, 1 - 34127 Trieste

Chemicals can come in contact with the skin, either in their bulk form or in a nanosize range (between 1 and 100 nm), and there are already many applications of various metal nanoparticles (MNPs) in dermatology, such as photoprotection, in nanodiagnostics and biomedical sciences, engineering and nanotechnology, and in many new materials and innovative products [1]. A wide debate concerning the ways of MNPs interaction with the skin, oral mucosa and other membranes (i.e. meningeal ones) and the relative potential health risks is ongoing in the scientific community.
In this communication recent results on skin permeation of different metal-containing nanoparticles (Ag, Au, Pt, Rh, Pd, Ni, Co_3O_4 and TiO_2) are presented paying particular attention to multi-analytical approach using ICP-MS, ICP-AES, TEM, SEM-EDX, AFM techniques and synchrotron radiation computed microtomography.
Ion formation is a crucial point, because MNPs can release a greater amount of ions compared to bulk material, due to their high surface/mass ratio. Furthermore some MNPs can reach the hair follicles and from there work as a long lasting reservoir for ions release. A prolonged metal release could increase the risk of allergic contact dermatitis for NPs containing sensitizing metals, such as Ni, Pd and Co.
Within the limitations determined by the use of a specific permeation model, our preliminary findings allow to say that the examined biological membranes are not completely impermeable to MNPs [2-3].

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CALIBRATION TRANSFER BETWEEN NEAR-INFRARED SPECTROMETERS: A COMPREHENSIVE OVERVIEW

R. Vitale[1]
Grupo de Ingeniería Estadística Multivariante, Departamento de Estadística e Investigación Operativa Aplicadas y Calidad, Universitat Politècnica de València, Camino de Vera s/n, 46022, Valencia, Spain

Calibration transfer between near-infrared (NIR) spectrometers is a subtle issue in analytical chemistry. In fact, as even very similar instruments may generate strongly different spectral responses, regression models developed on a first NIR system can be rarely used with spectra collected by a second equipment [1]. In the scientific literature, several ways of addressing this issue have been described since early 90s, but nowadays such topic seems to be still extremely actual, especially from an industrial perspective, for its intrinsic economic repercussions [2-4].
This work aims at providing a comprehensive overview of the calibration transfer problem and will try to answer the following questions:

1. When and why should calibration transfer be performed?
2. How can calibration transfer be carried out? Should we operate either on the spectral data or on the regression model coefficients?
3. Which are the pros and cons of the different calibration transfer strategies?

Recent proposals and new contributions to the field will be also presented, which will show how calibration transfer has recently gained new life for both spectroscopists and chemometricians [5].

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Oral Communications

HEAVY METAL SORPTION BY WATER KEFIR IN DIFFERENT CONDITIONS

M. Cantamessa[1], M. Ginepro[1], V. Turone[1], G. Volpi[1], V. Zelano[1]
[1]Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria 7 – 10125 Torino

"Water kefir" is a fermented drink with an acidic, sweet and alcoholic taste. It is obtained from sugary solutions after 24-48 hours of fermentation by water kefir grains. Previous works established that these grains are composed principally by lactic and acetic bacteria and yeasts on a polysaccharide. Each colony has many different microbial species that give it peculiar characteristics. Water kefir beverage is used as a dietary supplement, to rebalance the intestinal microflora. [1]
Due to their structure and functional groups, water kefir colonies could interact with heavy metal both physically and chemically. As a result of the increasing anthropic activities, the possibility of heavy metal contamination in food and water is high. So it is important to determine the chemical quality of water, particularly the heavy metal content, in order to evaluate the possible human health risk.
In this work, heavy metal concentrations have been evaluated in a water kefir fermentation process as a function of time (24, 48, 72 hours) and content of sucrose (0-5%) and heavy metals (kefir grains/metal solution ratio 1:10 and 1:1), at different starting pH (3.5, 4.5, 6) and with different buffer type (citrate and acetate $5 \cdot 10^{-3}$ M). Two different colonies purchased from private sellers were tested. The determination of Cr, Mn, Co, Ni, Cu, Cd, Pb, Ba, Na, K, Mg, Ca in water kefir beverages was made by ICP-OES. The pH value was constantly monitored. [2,3]
The aim of this work was to understand if water kefir grains used for homemade beverage could decrease the water heavy metal content and in which experimental conditions.
Among the tested experimental conditions, the best combination is: sucrose 5%, 24 hours, pH=4.5, acetate buffer, kefir grains/metal solution ratio 1:1. In these conditions, the heavy metal abatement by water kefir is particularly effective for Cr, Pb (approx. 70%) and good for Cu, Ni, Mn (approx. 50%).
In conclusion, water kefir grains revealed to be an efficient metal adsorber/biosorber in the studied conditions. The proposed study represents an efficient procedure to determine the metal abatement degree due to water kefir grains activity. Heavy metal polluted water can be partially purified during the water kefir fermentation process in the simulated conditions.

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INVESTIGATION BY RESPONSE SURFACE METHODOLOGY OF EXTRACTION OF CURCUMINOIDS FROM TURMERIC WITH ETHYL LACTATE AND MIXTURES OF BIOCOMPATIBLE SOLVENTS

A.A. D'Archivio[1], M. A. Maggi[2], F. Ruggieri[1]
[1]Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila, Via Vetoio, 67010 Coppito, L'Aquila, Italy
[2]Hortus Novus, Via Collepietro, 67100 L'Aquila, Italy

The yellow-orange polyphenols curcumin (CUR), demethoxycurcumin (DEM) and bisdemethoxycurcumin (BIS), known as curcuminoids, are the major bioactive constituents of turmeric (the dried ground rhizome of Curcuma longa L.). Therapeutic properties of CUR and its derivatives, including anti-cancer, anti-oxidant, anti-inflammatory and anti-microbic, have been investigated in recent years. However, low solubility and poor stability of curcuminoids in aqueous solutions can severely limit their application as drugs or functional food additives. Ethyl lactate (EL) is an environmentally friendly solvent since is completely biodegradable, non-corrosive and non-ozone-depleting. It is miscible with both water and hydrophobic liquids and exhibit excellent solvent properties. Due to its low toxicity, use of EL in food and pharmaceutical products has been approved by both the US Food and Drug Administration and the European Union.
In the present work, high-performance liquid-chromatography (HPLC) was applied to investigate potentiality of EL as a solvent for the extraction of the curcuminoids from turmeric. In addition to the pure EL, we evaluated solubilisation capability of binary and ternary mixtures of EL, water and ethanol, these being the only solvents accepted in food industry and medicine. Response surface methodology combined with a three-component mixture design of experiments was applied to investigate the extraction efficiency in the whole composition range. Moreover, stability of CUR and its analogues in the extraction media has been investigated by HPLC measurements.

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ELECTRONIC TONGUE AND ELECTRONIC EYE FOR MONITORING MATURATION LEVEL OF GRAPES

L. Pigani[1], G. Vasile Simone[1], G. Foca[2], A. Ulrici[2], F. Masino[2], R. Seeber[1]
[1]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia, Via G. Campi, 103 – 41125 Modena
[b]Dipartimento di Scienze della Vita, Università di Modena e Reggio Emilia, Padiglione Besta, Via Amendola, 2 – 42122 Reggio Emilia

The development of analytical procedures for the determination of fruits quality, meeting the requirement of simple instrumentation and rapid execution and response, is functional to several steps of the production chain, from the selection during the harvest to the evaluation of the storage conditions.
Monitoring of the maturation level of grapes constitutes the essential task for planning the harvest and the final oenological result depends primarily on the assessment of grape ripeness. For the evaluation of the different types of maturity such as technological, phenolic and aromatic, the quantitative determination of specific analytical parameters, including sugar and acid contents, polyphenols and aroma compounds is necessary. Therefore, the development of effective new devices and methods suitable for fast detection, for operating on small amounts of samples, possibly requiring minimal or no sample pretreatment is urgent.
The approach to this goal that we followed in our laboratories considers the use of both an electronic tongue (ET) and an electronic eye (EE). In particular in this report the results regarding the development and application of the ET in the analysis of different samples of grapes at different maturation levels will be shown. The ET used in this study consists of two different amperometric sensors, a Pt electrode modified by a conducting polymer and a sonogel carbon electrode, each one providing, in principle, different information. The relevant electrochemical signals have been elaborated through chemometric techniques. The relation between the information coming from the two different sensors and the chemical data (acidity, sugar content, polyphenolic composition, colour index) obtained through standard techniques can in principle allow the easy and objective evaluation of the maturation level of grapes. Following this approach, each electrochemical signal is considered as a sort of fingerprint of the analysed sample, supposed to bring the significant chemical information for the envisaged purpose.

DETERMINATION OF 7 TETRACYCLINES IN MILK AND EGGS BASED ON CONVENTIONAL HPLC/DAD USING A COLUMN PACKED WITH CORE-SHELL PARTICLES

S. Summa[1], A. Armentano[1], S. Lo Magro[1], D. Centonze[2], M. Muscarella[1]
[1] Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata, Via Manfredonia,20 -71121 Foggia
[2]Dipartimento di Scienze Agrarie, degli Alimenti e dell'Ambiente e CSRA, Università degli studi di Foggia, via Napoli, 25, 71121 Foggia

Tetracyclines (TCs) are important group of antibiotics used in veterinary medicine. They are given to farm animals to not only prevent and treat diseases but also to fraudulent purposes. The inappropriate and uncontrolled use of these substances may result in the presence of their residues in food such as eggs and milk. These can represent a serious risk for the human health due to the toxic, allergic effects and antibiotic resistance. The Regulation 37/2010/EU establishes the maximum residue limits (MRLs) of 100 µg/kg and 200 µg/kg for TCs in milk and eggs, respectively. These MRLs are expressed as the sum of the parent drug and its 4-epimer, except for doxycycline. Since under mild acid conditions, the parent TCs reversibly covert into the 4–epimers, there is the need to develop methods able to determine both molecular forms. High Performance Liquid Chromatographic (HPLC) methods combined with diode array detection (DAD) and mass spectrometry (MS) are commonly used to confirm the presence of these drugs in different food matrices. Several chromatographic methods have been proposed to determine TCs using traditional columns with 5 µm particles [1]. Many of them are able to detect the parent TCs, and only few methods include the determination of their epimers, which represents a challenge for the chromatographic separation. At the best of our knowledge, new columns packed with core-shell particles are not largely used for the detection of TCs in food. In order to obtain the separation of the seven TCs reported in the 37/2010/EU in a reasonable time and improve the chromatographic efficiency, a new method based on the use of core-shell column on HPLC with DAD detection for the research of TCs in milk and eggs is here described. The use of this new stationary phase on conventional HPLC system was possible without any up-grade on the experimental set-up. The optimised chromatographic conditions allow the separation of the TCs and their epimers in about 10 minutes. The sample preparation offers a good compromise between recovery and specificity, as demonstrated by the preliminary validation studies.

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QUALITY ASSESSMENT AND AUTHENTICITY OF ITALIAN AND SERBIAN WINES

P. Fermo[1], G. Giannelli[1], A. Mangone[2], Ž. Tešic[3]
[1]Dipartimento di Chimica, Università degli Studi di Milano, Via Camillo Golgi, 19 – 20122 Milano
[2]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via Edoardo Orabona, 4 – 70125 Bari
[3]University of Belgrade (Serbia), Faculty of Chemistry

This work aims to the collection of a large dataset referring to the chemical composition of wines coming from different areas both Italian and European. In particular wines coming from Friuli Venezia - Giulia, Veneto, Umbria and Serbia have been analyzed.
The information obtained through the analysis of wines will be integrated with the one coming from the analysis of soil and plant parts such as leaves and grape skin, pulp and seeds.
Wine is a premier agricultural product of the EU and exported worldwide. In Italy, among the food products, wine is of great value and as a consequence it is of crucial importance to keep up its reputation. The Serbian wine industry is experiencing significant growth. Sugaring, watering and counterfeit are malpractices that may undermine the position of wine on both internal and international markets. Furthermore the assessment of the wine authenticity and of its quality is of priority importance from the economical point of view and also because of the health benefits. Authenticity is an important tool for traceability, food safety and quality control of foodstuffs.
From the instrumental point of view several techniques have been used in order to collect as many information as possible: FAAS, ICP-MS for the determination of metal content and HPLC - LTQ - Orbitrap for polyphenolic compounds such as flavonoids and anthocyanins. The data collected will provide a solid ground on which build a database for authenticity and origin studies.
Multivariate statistical procedures (PCA, HCA and classification methods), in order to efficiently extract the maximum useful information from experimental results, will be applied. As a final goal the methodological set-up will be applied to the comparative assessment of wine varieties from both Italian and Serbian local winemakers.
At this stage the work is especially focusing on metals analysis: the results obtained are very promising in terms of authenticity and contamination and suggest a good correlation between some metal level and both type of wine and geographical origin.

SIZE RESOLVED METAL DISTRIBUTION IN THE PM MATTER OF THE CITY OF TURIN (ITALY)

V. Maurino[1], M. Malandrino[1], M. Casazza[2], O. Abollino[1], C. Minero[1]
[1]1 Università degli Studi di Torino, Dipartimento di Chimica, Via P. Giuria 5, 10125, Torino, Italy
[2] University 'Parthenope' of Napoli, Department of Science and Technologies, Centro Direzionale, Isola C4, 80143, Napoli, Italy

A work on the characterization of the air quality in the city of Turin was carried out in different sampling periods, reflecting late summer and winter conditions, including a snow episode during the early 2012 european cold wave.
The concentrations of 16 elements in eight size fractions of the aerosol were determined using inductively coupled plasma-mass spectrometry. The collection was carried out with a Andersen MkII cascade impactor.
The size distribution of elements allowed the identification of three main behavioural types: (a) elements associated with coarse particles (Cd, Cr, Cu, Fe, Mn, Mo, Pt and Sn); (b) elements found within fine particles (As, Co, Pb and V) and (c) elements spread throughout the entire size range (Ni, Pd, Rh and Zn).
Principal Component Analysis allowed to examine the relationships between the inorganic elements and to infer about their origin. Chemometric investigation and assessment of similarity in the distribution led to similar conclusions on the sources.
The concentration of gaseous trace pollutants (O3, NOx and VOCs) was determined. The concentrations of these pollutants are scarcely correlated with the metal contents of all the size classes of the PM. The differences found in the O3, NO2 and VOCs levels of the two winter campaigns due to the high photochemical reactivity in the period after the snow episode, do not reflect in differences in the metals distribution in the PM. Since PM metals, NOx and VOC have common sources, this behaviour is due to relevant differences in the transformation and deposition processes.

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CHEMICAL CHARACTERIZATION OF COARSE AND FINE FRACTION OF PM SAMPLES OF A RURAL SITE OF SOUTH ITALY

A. Genga[1], B. Introna[1], M. Siciliano[1], T. Siciliano[2], C. Malitesta[1]
[1]Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Lecce,73100, Italy
[2]Dipartimento di Beni Culturali, Università del Salento, Università del Salento, Lecce,73100, Italy

The concentration of atmospheric particulate matter is key concerns in several urban and suburban areas in Europe. In the last few years, knowledge of the chemical composition of airborne particulate matter (PM) and the necessity of differentiating PM components with respect to both health and environmental effects have been recognised as increasingly important within the scientific community.
In this work we present the results of a summer-autumn sampling campaign during 2015 in a rural site of south Italy. We collect PM10 and PM2.5 samples every 24 hours and in order to better understand the processes affecting the chemistry of the atmosphere we also collect PM2.5 every 6 hours.
Soluble ionic species (major ions: SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, $C_2O_4^{2-}$, Na^+, K^+, Mg^{2+}, Ca^{2+}), 12 elements (Ni, Cu, V, Mn, As, Pb, Cr, Sb, Fe, Al, Zn and Ti) and OC and EC contents are analyzed.
The analysis of the content of heavy metals and water-soluble salts was performed on Teflon filters, while the determination of the OC and EC was performed on the quartz membrane after a thermic treatment.
Multivariate Statistical treatments of data have been tested on PM10 and PM2.5 separately and then together in order to evaluate the informations reached with the merging of the data. After all the PM2.5 samples collected at higher time frequency have been evaluated.

SUPRAMOLECULAR DETECTION OF BTEX IN AIR: FROM SPME COATINGS TO MINIATURIZED MEMS SENSORS

F. Bianchi, N. Riboni, F. Bertani, E. Dalcanale, M. Careri
Dipartimento di Chimica, Università di Parma, Parco Area delle Scienze 17/A, 43124 Parma

Monitoring air pollution in urban and industrial areas requires the design of new air quality control systems capable of monitoring dangerous pollutants at trace concentrations. The detection of airborne aromatic hydrocarbons is a longstanding problem due to the need of determining low benzene levels in the presence of overwhelming amounts of water and other hydrocarbons. Pre-concentration is the most used approach for BTEX enrichment both in urban and indoor air. Major drawbacks of this approach are related both to lack of selectivity and to the use of time-consuming procedures. Owing to its simplicity, possible automation and low cost, solid phase microextraction (SPME) is an attractive alternative to most of the conventional sampling technologies [1]. A conformationally mobile tetraquinoxaline-bridged cavitand (QxCav) has been already proposed by our research group as adsorbent material [2,3] for the selective sampling of BTEX from water samples. Rational design of QxCav molecular structures offers the possibility for further improving sensitivity and selectivity of the preconcentration step. To enhance both selectivity and sensitivity of BTEX detection we present novel SPME coatings based on both rigid QxCav receptors and a new class of triptycene tetraquinoxaline "roofed cavitands". The proposed cavitands are compared to the commonly used commercial fiber coatings in terms of thermal stability, film thickness, enrichment factor and selectivity. The selective enrichment of BTEX is demonstrated in real-world air samples. Finally, the best receptor will be used to develop a microelectromechanical sensor for the on-line measurement of benzene in air.

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DETERMINATION OF CYANIDE IN SOILBY PENTAFLUOROBENZYL ALKYLATION AND GC/MS ANALYSIS

B. Campanella[1,2], L. Biancalana[1], M. Onor[2], E. Bramanti[2], A. D'Ulivo[2], Z. Mester[3], E. Pagliano[3]
[1]Istituto di Chimica dei Composti Organometallici - UOS di Pisa,Consiglio Nazionale delle Ricerche (CNR), Via Moruzzi 1 – 56124 Pisa
[2]Dipartimento di Chimica e Chimica Industriale,Università di Pisa, via Moruzzi 13 – 56124 Pisa
[3]National Research Council of Canada, 1200 Montreal Road, Ottawa, ON K1A 0R6, Canada

As a result of increased industrial activities and waste disposal, soils available for cultivation and farming are nowadays becoming contaminated with toxic compounds. Cyanide and its derivates are well known powerful toxic agents for mammals, and their relevant industrial use has kept alive the interest for the development of straightforward analytical methods for their determination.[1]
We developed a novel method for the determination of cyanide in soil based on a single-step derivatization with pentafluorobenzyl bromide (PFB-Br) followed by identification with gas chromatography – negative chemical ionization mass spectrometry. Despite of alkylation with PFB-Br is a well known derivatization strategy for the analysis of anions, here innovative aspects of this reactionare presented. The effects of some parameters on the derivatization step were established in order to achieve the selective formation of the trialkylated nitrile, $(C_6F_5CH_2)_2C(C_6F_5)CN$.
Asimple and time-saving configuration based on a micro-distillation strategy was developed for cyanide extraction from soil, to guarantee operator safety along with matrix removal. This procedure allows a one-step matrix separation and the analyte preconcentration combined with a quantitative recovery.
The method was applied to the analysis of total and free cyanide in two certified reference materials of contaminated soil by isotope dilution analysis using $K^{13}C^{15}N$ as internal standard.

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A MULTI-TECHNIQUE APPROACH FOR THE CHARACTERIZATION OF PM 2.5 DUE TO BIOMASS COMBUSTION

P. Fermo[2], D. Atzei[1], M. Fantauzzi[1], L. Corbella[2], R. Vecchi[3], G. Valli[3], A. Rossi[1]
[1]Dipartimento di Scienze Chimiche e Geologiche - Università di Cagliari - Cittadella Universitaria di Monserrato 09042 Monserrato (Cagliari)
[2]Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi, 19 – 20122 Milano
[3] Dipartimento di Fisica, Università degli Studi di Milano, Via G. Celoria, 16 – 20122 Milano

The present work aims to evaluate the contribution of wood combustion to particulate matter emissions (PM2.5) in the rural village of Gonnostramatza (West Sardinia, Oristano, Sardinia) where firewood is largely employed for domestic heating. Gonnostramatza has about 950 inhabitants and is located at an altitude of 110 m a.s.l. in a rural area isolated from other urban centres. It represents an ideal case study for the evaluation of the impact of biomass burning on PM emissions. Two sampling campaigns were carried out: one in winter (December 2014- January 2015) and one in summer (June 2015). During winter, 30filters were collected sampling on alternate days on quartz fibres and on Teflon filters while during summer 15 filters were collected with the same criterion (8quartz and 7 Teflon).
Ion chromatography (IC) has been employed for the quantification of the main cations: Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+, and anions: NO_3^-, NO_2^-, SO_4^{2-}, Cl^-, acetate, propionate, formiate, methansulphonate. Furthermore levoglucosan, the specific marker used to evaluate the contribution of biomass burning to PM emissions [1], was quantified by HPAEC–PAD (high-performance anion-exchange chromatography with pulsed amperometric detection). Organic Carbon (OC) and elemental carbon (EC) were determined by TOT (Thermal Optical Transmittance). Elemental analysis was carried out by energy-dispersive X –ray fluorescence (ED - XRF) and by X-ray photoelectron spectroscopy (XPS). The last was exploited on samples collected on PTFE for shedding light on the surface composition of the particulate and to compare the results with those obtained by the other techniques.
PM average concentration during wintertime was 15.3 (8.4) $\mu g*m^{-3}$ while OC and EC were 8.1 (3.8) $\mu g*m^{-3}$ and 3.7 (0.4) $\mu g*m^{-3}$ respectively. The high concentrations of levoglucosan, on average 2.1 (1.2) $\mu g*m^{-3}$, demonstrate the important contribution of biomass burning to PM emission during winter. It is also worth noting that the carbon content of levoglucosan accounts for the 11.5% of OC. Less than 2% of OC is due to some short chain organic acids such as acetate and formiate while the remaining part is due to other organic

substances both of primary or secondary origin in part also due to biomass combustion. Among cations K^+ has the highest concentration and during winter it shows a very good correlation with levoglucosan, as expected. During summer all the main PM constituents were present at lower concentrations and the contribution of wood combustion was not evidenced. A clear decrease of PM mass during windy days was found thus indicating the correlation to meteorological parameters. XPS surveys showed the presence of C, N, O and S. C1s has a complex shape and it could be resolved in its components according to [2]. The speciation of carbon will be presented and discussed together with the data obtained by the other methods.

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BIOMARKERS IN LACUSTRINE SEDIMENT CORES FOR RECONSTRUCTING EARLY HUMAN ACTIVITY AND FIRE HISTORY

Battistel D.[1,2], Kehrwald N.M.[3], Kirchgeorg T.[1], Argiriadis E.[1], Callegaro A.[1], Barbante C.[1,2]

[1]Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Cà Foscari Venezia, Via Torino, 155 – 30702 Mestre Venezia
[2]Institute for the Dynamics of Environmental Processes, IDPA-CNR, Via Torino, 155 – 30702 Mestre Venezia
[3]U.S. Geological Survey, Geosciences and Environmental Change Science Center, Lakewood, CO 80225, USA

Even before the Industrial Revolution, human activity associated with the development of agriculture and biomass burning for slush-and-burn practises could have had an impact on the environment and the climate system. However, the timing of the development of human settlements had been asynchronous around the world and had covered areas with different extents, making it difficult to disentangling the anthropogenic contribution from natural forcing to the environment and climate system. The use of specific molecular markers in sediment cores is a powerful strategy for reconstructing human presence and fire activity at local scale. Indeed, faecal sterols (5β-cholestan-3β-ol) can be associated with humans, while levoglucosan (1,6-anhydro-β-D-glucopyranose) and polycyclic aromatic hydrocarbons (PAHs) can be used for reconstructing fire history. Biomarker records, determined by using GC/MS, successfully integrate archaeological evidence, environmental and climatic reconstructions.
Three different sites were analyzed and herein considered. First, the early impact of Polynesian arrival in New Zealand since ~1260 A.D. that triggered an initial burning period that, in turn, led to the forest biomes conversion to open shrub-lands. This study was performed analyzing sediments from Lake Kirkpatrick (NZ) and showed that a small population is able to instigate a widespread and permanent environmental change.
Different dynamics were observed during the Iron Age (1100-2400 A.D.) in East Africa. In this case, form Lake Victoria sediment cores analysis, the development of human settlements seems a consequence rather than a cause of the environmental changes that are mainly due to climatic forcing.
Finally, by the analysis of Lake Trasimeno (Italy) sediment core, we reconstructed the development of human settlements around the lake, since the Etruscan-Roman period (~3000 yrs BP). This record showed a more complex human-fire-climate relation.

MAJOR AND MINOR ELEMENTS IN THERMOCHEMICAL CONVERSION OF BIOMASS

J. Tafur-Marinos, S. Barbero, M. Ginepro, V. Zelano
Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria, 7 – 10125 Torino.

Thermochemical biomass conversion includes a number of possible roots to produce useful fuels from the initial biomass feedstock. The base of thermochemical conversion is the pyrolysis process, which includes all chemical changes occurring when heat is applied to a material in the absence of oxygen. An extension of pyrolysis is the gasification, a thermal process with partial oxidation optimized to give an gas combustible[1].
Biomasses have different contents of elements, such as alkali and alkaline earth metals that may cause problems to the plant system, and heavy metals harmful for environment [2].
The aim of this work is to see how the metal contents of char (carbonaceous residue) change according to different conversion temperatures and elements properties, in order to evaluate which elements present in the initial biomass will find partly or totally in the char.
To this end, major and minor elements were determined in biomass (conifer pellets and spruce) and their chars produced in laboratory and industrial plants. In laboratory, the conifer pellets were pyrolysed at 550 °C, while spruce at 400, 550 and 1100 °C.
The analyses were made by ICP-OES (Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si and Zn), CVAAS (Hg) and HGASS (As).
The results of laboratory pyrolysis show that, in general, the concentration of the elements increases with temperature due to the decrease of the carbonaceous matrix. However, some deviations are present depending on the properties of the elements (eg. Cd, Pb, S).
Moreover, the data comparison between the industrial pyro-gasification char and pyrolysis char (550 °C) reveals that many elements have higher concentrations in pyro-gasification char. Also, the comparison between industrial pyrolysis char and pyrolysis char (550 °C) has a similar trend.
Therefore, the results showed that the behaviour of elements is affected by their properties and the thermochemical process used (pyrolysis vs gasification).

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TRACE AND RARE EARTH ELEMENTS IN PM_{10} COLLECTED AT NY-ÅLESUND (SVALBARD ISLANDS, ARCTICA)

M. Malandrino[1], O. Abollino[1], A. Giacomino[2], S. Buoso[1], E. Conca[1], R. Udisti[3]
[1]Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria, 5 – 10125 Torino
[2]Dipartimento di Scienze e Tecnologia del Farmaco, Università degli Studi di Torino, Via Pietro Giuria, 9 – 10125 Torino
[3]Dipartimento di Chimica, Università degli Studi di Firenze, Via della Lastruccia, 3 – 50019, Sesto Fiorentino

The chemical composition of atmospheric aerosol is responsible for the impact of particulate matter on human health and, at a larger scale, on the ongoing climate changes.
The Arctic regions are showing to be the first areas affected by the present climatic variations. Consequently, the study of the chemical composition of atmospheric aerosol in the polar areas is important to understand the feedback processes between the climate forcing and the environmental responses [1, 2].
In this study, the concentrations of main and trace metals in the PM_{10} collected at Ny-Ålesund (Svalbard Islands) during the spring and summer 2010, 2011 and 2012 campaigns were determined. The results obtained reveal an evident seasonal pattern in the temporal profiles of the majority of the chemical components of the PM_{10}, that show higher atmospheric concentrations in March-April. The most likely explanation for this trend is the influence of continental sources on the composition of the Arctic PM_{10}. Indeed, Svalbard Islands are affected by aerosols coming from anthropized continental areas by long range transport processes, especially occurring in early spring.
The enrichment factors, calculated considering Al as a crustal reference element, are higher than 100 for Zn, Mo, As, Cd, Pb and Na, indicating their non- geogenic origin (anthropogenic sources and sea spray).
The final dataset was treated by chemometric techniques. Principal Component Analysis showed an evident separation between spring and summer Arctic PM_{10} samples. Factor Analysis identified four factors: F1 – geogenic source (Al, Fe, Mn, Ba, Ti and REEs with exception of Ce); F2 – sea spray source (K, Na and Mg); F3 – combustion processes source (As, Cd, Co, Ni, V, Pb and Zn); F4 – wear-related source (Cu, Zn and Ce).
This work was supported by MIUR and CNR funds and facilities.

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PRIMARY PRODUCTION, SEA ICE MELTING, AND BIOGENIC AEROSOL IN THE ARCTIC

S. Becagli[1], L. Lazzara[2], C. Marchese[3], S.E. Ascanius[4], M. Cacciani[5], L. Caiazzo[1],C. Di Biagio[6,7], T. Di Iorio[6], A. di Sarra[6], P. Eriksen[8], F. Fani[2], F. Giardi[1], D. Meloni[6], G. Muscari[9], G. Pace[6], M. Severi[1], R. Traversi[1], R. Udisti[1].
[1]Department of Chemistry, University of Florence, Via della Lastruccia 3, 50019 Sesto F.no, Florence, Italy
[2]Department of Biology, University of Florence, Via Madonna del piano 6, 50019 Sesto F.no, Florence, Italy
[3]Département de Biologie, Chimie et Géographie, Université du Québec à Rimouski, 300 Allée des Ursulines, Rimouski, Québec G5L 3A1, Canada
[4]Danish Meteorological Isntitute, Qaanaaq, Greenland
[5]Physics Department, Sapienza University of Rome, Italy
[6]ENEA, Laboratory for Earth Observations and Analyses, Rome, 00123, Italy.
[7]LISA, UMR CNRS 7583, Université Paris Est Créteil et Université Paris Diderot Institut Pierre Simon Laplace Créteil, France.
[8]Danish Meteorological Institute, Copenhagen, Denmark.
[9] Istituto Nazionale di Geofisica e Vulcanologia, INGV, Rome, 00143, Italy.

In this work we investigate the relationships linking methanesulfonic acid (MSA, arising from the atmospheric oxidation of the biogenic dimethylsulfide, DMS) in atmospheric aerosol, satellite-derived chlorophyll a (Chl-a), and oceanic primary production (PP), also as a function of sea ice melting (SIM) and extension of the ice free area in the marginal ice zone (IF-MIZ) in the Artic. MSA was determined in PM_{10} samples collected over the period 2010-2012 at two Arctic sites, Ny Ålesund (78.9°N, 11.9°E), Svalbard islands, and Thule Air Base (76.5°N, 68.8°W), Greenland. PP is calculated by means of a bio-optical, physiologically based, semi-analytical model in the potential source areas located in the surrounding oceanic regions. MSA shows a better correlation with PP than with Chl-a, besides, the source intensity (expressed by PP) is able to explain more than 30% of the MSA variability at the two sites; the other factors explaining the MSA variability are taxonomic differences in the phytoplanktonic assemblages, and transport processes from the DMS source areas to the sampling sites. The sea ice dynamic plays a key role in determining MSA concentration in the Arctic, and a good correlation between MSA and SIM and between MSA and IF-MIZ is found for the cases attributable to bloomings of diatoms in the MIZ. Such relationships are calculated by combining the data sets from the two sites and suggest that PP is related to sea ice melting and to the extension of marginal sea ice areas, and that these factors are the main drivers for MSA concentrations at the considered Arctic sites.

EVIDENCE OF THE LASCHAMP GEOMAGNETIC EXCURSION IN THE NITRATE RECORD FROM EPICA-DOME C ICE CORE

R. Traversi[1], S. Becagli[1], S. Poluianov[2], M. Severi[1], S.K. Solanki[3,4], I.G. Usoskin[2,5], R. Udisti[1]
[1]Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia, 3 - 50019, Sesto F.no, Firenze.
[2]ReSoLVE Center of Excellence, Faculty of Sciences, University of Oulu, PL 3000, FIN-90014 Finland
[3]Max-Planck-Institut für Sonnensystemforschung, Justus-von-Liebig-Weg 3, D-37077, Göttingen, Germany.
[4]School of Space Research, Kyung Hee University, Yongin, Gyeonggi, 446-701, South Korea.
[5]Sodankylä Geophysical Observatory, Oulu unit, FIN-90014 University of Oulu, Finland.

The potential of nitrate records from polar ice for obtaining paleoclimatic information has never been tested by a direct comparison with the established proxies of such variability measured along the same ice core. Here we present the first direct comparison of cosmogenic ^{10}Be and chemical parameters in the period of 38-45.5 kyr BP, spanning the Laschamp geomagnetic excursion (41 kyr BP) from the EPICA-Dome C (EDC) ice core. The Laschamp event was the most relevant excursion in the intensity of the geomagnetic field recorded by the Earth in the last 50 kyr.
A principal component analysis (PCA) allowed to identify and to group different components as a functions of the main sources, transport and deposition processes affecting the atmospheric aerosol at Dome C. The evident preferential association of 10Be with nitrate rather than with other chemical species, marks the presence of a distinct source, which we label as "cosmogenic". Moreover, a wavelet analysis highlighted the high coherence and in-phase relationship between ^{10}Be and nitrate around the Laschamp event. Both the PCA and wavelet analyses ruled out a significant role of calcium in driving the ^{10}Be and nitrate relationship, which is particularly relevant for a plateau site such as Dome C, especially given the high dust amount in the glacial period during which the Laschamp excursion took place. The evidence that the nitrate record from the EDC ice core is able to capture the Laschamp event confirms the potential of this marker for studying galactic cosmic ray flux variations and thus also major geomagnetic field excursions at pluri-centennial-millennial time scales, thus opening up new perspectives for this marker in paleoclimatic studies.

FIRST MEASUREMENTS OF TRACE METALS IN THE ATMOSPHERIC AEROSOL OF CENTRAL ANTARCTICA AT DOME C (CONCORDIA STATION)

C. Mantini, C. Truzzi, A. Annibaldi, S. Illuminati, G. Scarponi
Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, Via Brecce Bianche – 60100 Ancona

In this communication we report on the first measurements on the Cd, Pb and Cu traces in the atmospheric aerosol of Dome C (Concordia station), a remote site on the plateau of Central Antarctica, for which no data are available until now. Aerosol samples were collected during the Austral Summer 2005-2006 by PM10 high-volume impactors at two different sites: (i) immediately downwind of Concordia station, and (ii) near the Astrophysic Tent, a supposed "cleaner" site, ~800 m upwind of the Station. A differential weighing procedure was used on site to obtain the aerosol mass collected in each filter and then the aerosol concentration was available for each sample [1]. Metal contents were determined by an ultrasensitive electroanalytical technique, the Square Wave Anodic Stripping Voltammetry (SWASV) according to a procedure set up recently [2]. The availability of the aerosol mass in each sample allowed us to express results also in terms of mass fractions in the aerosol, as well as in the usual way of reporting atmospheric concentrations. Metal mass fractions, excluding two anomalous values, varied as follows (min-max): Cd 1.0-15.7 μg/g, Pb 96-200 μg/g, Cu 0.17-5.4 mg/g. In terms of atmospheric concentrations, the values were Cd 0.09-7.0 pg/m^3, Pb 12-62 pg/m^3, Cu 0.027-2.40 ng/m^3. The higher values were observed in the first part of the season, possibly in relation with the intense activity at Concordia station connected with the beginning of the expedition, including aircraft arrivals/departures. The effect of the wind direction was also observed. In particular, in the intermediate period of the campaign the wind direction was reversed for several days with respect to the prevailing one, and the metal contents, in particular Cd, decreased at Concordia station and increased at Astrophysic Tent. In general, there are no high differences in metal concentrations between samples collected near the station and those collected at the Astrophysic Tent. This result suggests that the human impact at Dome C influences, not only the zone very close to the station, but also the area in the neighborhood, including the "supposed clean" site of the Astrophysic Tent, indeed not so far.

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RECOVERING PALEO-RECORDS FROM ANTARCTIC ICE-CORES BY COUPLING A CONTINUOUS MELTING DEVICE AND FAST ION CHROMATOGRAPHY.

M. Severi, S. Becagli, L. Caiazzo, F. Giardi, M. Marconi, R. Traversi, R. Udisti.
Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia, 3 - 50019, Sesto F.no, Firenze.

The increasing interest in the understanding of global climatic changes and on natural processes related to climate yielded the development and improvement of new analytical methods for the analysis of environmental samples. The determination of trace chemical species is a useful tool in paleoclimatology, and the techniques for the analysis of ice cores have evolved during the past few years from laborious measurements on discrete samples to continuous techniques allowing higher temporal resolution, higher sensitivity and, above all, higher throughput. Two fast ion chromatographic (FIC) methods are presented. The first method was able to measure chloride, nitrate and sulfate in a melter-based continuous flow system separating the three analytes in just 1 min. The second method (called Ultra-FIC) was able to perform a single chromatographic analysis in just 30 seconds and the resulting sampling resolution was 1.0 cm with a typical melting rate of 4.0 cm min^{-1}. Both methods combine the accuracy, precision, and low detection limits of ion chromatography with the enhanced speed and high depth resolution of continuous melting systems. Both methods have been tested and validated with the analysis of several hundred meters of different ice cores. In particular, the Ultra-FIC method was used to reconstruct the high-resolution sulfate profile of the last 10 000 years for the EDML ice core, allowing the counting of the annual layers, which represents a key point in dating these kind of natural archives. The other method was largely used to reconstruct the paleo-volcanism on global and regional scale in three deep ice cores (EPICA Dome C, EPICA Dronning Maud Land and TALDICE), allowing to obtain precious information about the volcanic forcing on the climatic system.

PHOTOTRANSFORMATION OF PYRIDINIUM-BASED IONIC LIQUIDS IN WATER.

P. Calza[1], D. Vione[1], D. Fabbri[1], G. Noè[1], C. Medana[2], C. Minero[1].
[1]Dipartimento di Chimica, Università di Torino, Via P. Giuria, 5 – 10125 Torino
[2]Dipartimento di Biotecnologie Molecolari e Scienze per la salute, Università di Torino, via P. Giuria, 5 – 10125 Torino

Ionic liquid (ILs) are organic salts with a low melting point (<100 °C) that have been the object of several studies and industrial applications in the last years due to their unique physico-chemical properties. The low vapor pressure and flammability, the chemical and thermal stability, the high ionic conductivity, the wide electrochemical potential window and the ability to behave as catalysts make ILs useful for many applications, in particular as "green chemistry" replacements to traditional solvents. Although there is limited environmental data about these new "green solvents", the low biodegradability and considerable ecotoxicity of some of them underscore the importance to prevent ILs leakage into the environment and to develop effective means of removal and recovery from wastewaters. Taking into account the growing industrial interest and the potential threat to aquatic and terrestrial ecosystems, ILs are included in the list of the so-called "contaminants on the horizon".
In this work we compare four ILs (1-butylpyridinium bromide, BPy, 1-ethylpyridinium tetrafluoroborate, EPy, 1-(3-cyanopropyl)pyridinium chloride, CPy, and 1-butyl-4-methylpyridinium tetrafluoroborate, BMPy) by studying their overall photochemical fate and persistence by both direct and indirect photolysis. We evaluated substrate disappearance, evolution of transformation products (TPs), degree of mineralization and toxicity of the irradiated systems. The presence of different substituents, the alkyl chain length and the kind of inorganic anion influence the degradation kinetics and pathway. For instance, ~60% BPy was abated after 3 days irradiation, while only 20% EPy was removed after 7 days. The formed TPs were identified and characterized via HPLC-HRMS and, based on the overall data, a mechanism of phototransformation was proposed for the ILs examined.
Acute toxicity, evaluated with *Vibrio fischeri* bacteria, was initially very low but the phototransformation of CPy and BMPy yielded harmful compounds that caused inhibition of the bacteria luminescence. For three of the studied ILs it was possible to simulate the photochemical transformation kinetics and pathways in surface waters (direct photolysis, reaction with $^{\bullet}OH$ and with the triplet states of chromophoric dissolved organic matter), to assess their persistence in sunlit water bodies such as rivers or lakes.

BIODEGRADATION OF ANTHRACENE BY CHITOSAN MACROPARTICLES IMMOBILIZED LACCASE

A. Apriceno, A. M. Girelli
Dipartimento di Chimica, Università La Sapienza , P.le A.Moro, 5 - 00185 Roma

Polycyclic aromatic hydrocarbons (PAHs) are known to be toxic, mutagenic and/or carcinogenic and their contamination of soils and aquifer is of great environmental concern. Enzyme-based bioremediation of PAHs has increasingly been received attention and laccase is one of the most promising remedial enzymes [1].
Laccase (EC 1.10.3.2), a multicopper oxidases, catalyzes mainly the oxidation of phenolic substrates and the substrate range can be further extended to non phenolic compounds by using radical mediators such as *N*-hydroxybenzotriazole (HBT) [2] and 2,2-azinobis(3-ethylbenzothiazoline-6-sulfonate (ABTS) [3].
The immobilization of enzymes to water insoluble supports can increase their operational stability and durability and allows easy separation from the reaction medium and potential reuse of the biocatalysts.
Some recent studies focused on the degradation of PAHs by immobilized laccase on functionalized nanoparticles or kaolinite [4-6] however no researches have been done using macro particles supports.
The aim of this work is to develop a *Trametes versicolor* laccase-chitosan beads system in order to evaluate the degradation of an anthracene aqueous solution. Chitosan macroparticles have been prepared by precipitation in a NaOH solution and glutaraldehyde was chosen as crosslinking agent for binding covalently the enzyme. Support functionalization was verified by using Fourier Transform Infrared Spectroscopy (FTIR), elemental and thermogravimetric analysis. pH, T, glutaraldehyde and laccase concentrations were studied as parameters influencing enzymatic activity in order to improve immobilization yield.
Anthracene degradation, in presence of ABTS as mediator, was investigated at two different pH values, 5 and 7, using HPLC and an UV-Vis detector at 254 nm. Oxidation reaction of hydrocarbon was followed through either the product formation, 9,10-anthraquinone, and the contaminant decreasing in solution.
Pure chitosan beads were used as control to evaluate any possible interaction of anthracene with support.

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COMPETITIVE ADSORPTION OF VOCs FROM AQUEOUS SOLUTIONS ON HYDROPHOBIC ZEOLITES

E. Sarti[1], L. Pasti[1], A. Cavazzini[1], A. Martucci[2], E. Rodeghero[2], R. Bagatin[3]
[1] Department of Chemical and Pharmaceutical Sciences, University of Ferrara, Via L. Borsari 46 - 44121 Ferrara (Italy)
[2] Department of Physics and Earth Sciences, University of Ferrara, Via G. Saragat 1 - 44122 Ferrara (Italy)
[3] Research Center for Non-Conventional Energy, Istituto Eni Donegani Environmental Technologies, Via Maritano 26 - 20097 San Donato Milanese (MI, Italy)

Volatile Organic Compounds (VOCs) are water pollutants of concern, due to their widespread occurrence in natural and drinking waters and to their adverse effects on human health [1]. The adsorption efficiency of hydrophobic zeolites toward unary mixtures of VOCs in water has already been proved [2-3]. Different contaminants have been investigated (i. e. methyl tert-butyl ether, toluene, 1,2-dichloroethane and chlorobenzene) which were selected to represent different VOC classes: oxygenated, aromatics, chlorinated aliphatics and chlorinated aromatics, respectively. Since usually multiple pollutants coexist in the environment, the quantification of competitive interactions is important to predict the adsorption capability of materials for complex aqueous mixtures. This study aims to evaluate the adsorption of binary mixtures of VOCs in aqueous solutions on a commercial hydrophobic zeolite ZSM-5. To investigate the kinetics and the thermodynamics of the adsorption process, equilibrium measurements were carried under different operative conditions and structural analysis was performed on the loaded zeolite. The results showed that the adsorption capabilities of ZSM-5 for all the compounds were reduced in the presence of a second component in the mixture, in comparison with the single-component data, indicating a competitive adsorption. The binary system was described by a competitive dual site Langmuir adsorption isotherm, according to the results obtained by structural analysis. It has been found that each site inside the zeolite framework cannot be occupied simultaneously by more than one component, because of the short intermolecular distances among the adsorption sites.

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MODERN INKS ANALYSIS AND CONSERVATION PROBLEMS: CASE STUDIES

G. Germinario[1], I. D. van der Werf[1,2], A. Mirabile[3], L. Sabbatini[1,2]
[1]Dipartimento di Chimica, Università degli Studi di Bari, Bari, Apulia, 70125, Italy
[2]Centro interdipartimentale "Laboratorio di ricerca per la diagnostica dei Beni Culturali", Università degli Studi di Bari Aldo Moro, Bari, Apulia, 70125, Italy
[3]Paper conservator, 11 rue de Bellefond, Paris, 75009, France

Inks of felt-tip pens used by modern artists for the realization of sketches, drawings, copies, architectural drawings and other technical designs, have been comprehensively investigated by using a multi-technique approach. Inks are usually very sensitive to light and chemical agents and the exact knowledge of their composition may be important to define the optimal conservation treatment and/or storage conditions. So far, few studies have been addressed to the chemical characterisation of these materials [1] and often information on binders, fillers, dyes and pigments is lacking. Felt tip pens used by Lina Bo Bardi, Anne Floris Cabanis and commercial specimens of the Stabilo brand have been analysed with scanning electron microscopy (SEM), X-ray fluorescence (XRF), Fourier transform infrared (FTIR) and Raman spectroscopy, and pyrolysis/gas chromatography-mass spectrometry (Py-GC/MS). In this lecture results obtained with Py/GC-MS and Raman are reported. In some cases the dyes mixtures of inks have been separated by thin layer chromatography (TLC) before Raman analysis and pigments and dyes identification was fundamental in the interpretation of the pyrolytic fragmentation. Moreover, on samples where pyrograms suggested the occurrence of polysaccharides, GC/MS analyses were carried out to determine the sugar composition.
As a result, the study allowed to determine the chemical formulation of the inks, evidencing the use of an ample variety of dyes and pigments, different kind of binders, solvents and plasticizers.

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APPLICATION OF A REAL TIME MONITORING TOOL WITH ELECTROCHEMICAL DETECTION: A CASE STUDY

L. Micheli[1], C. Mazzuca[1], S. Dominijanni [2], S. Puteo [2], S. Sotgiu[2], S. Iannuccelli[2], A. Palleschi[1], G. Palleschi[1]
[1] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133, Rome, Italy
[2]Istituto centrale per il restauro e la conservazione del patrimonio archivistico e librario, Via Milano 76, 00184, Rome, Italy

The use of rigid gel based on the deacylated polysaccharide Gellan gum and calcium acetate (Gg) has been recently assessed to be as a new efficient wet cleaning agent for paper samples. Thanks to a fruitful cooperation with the ICRCPAL (Istituto Centrale per il Restauro e la Conservazione del Patrimonio Archivistico e Librario), we are developing an efficient and simple method to load Gellan gels with enzymes, obtaining "enzymatic Gellan gels" to remove lining and adhesive residues from paper supports [1]. The ICRCPAL has been developing wet treatments on work of art papers (Corretto?) using rigid Gellan gel, able to gradually release water and also to absorb water-soluble degradation products present on the paper. In this work we will present the results obtained on the last topic and then show its application in the case study of the engraving "The Wedding of Cupid and Psyche" (Diana Scultori, 1547-1612). The artwork was affected by a structural and chromatic deterioration due to a strong oxidative degradation mainly due to a previous lining intervention. The first wet cleaning treatment was monitored by means of a non invasive cleaning and diagnostic tool, based on a Gellan gum hydrogel combined with an electrochemical sensor. This system is suitable to verify *in situ* and in a simple way the efficiency of the cleaning treatment and to monitor the end of the procedure?? ?? [2]. After having identified the adhesive used to line "The Wedding of Cupid and Psyche" (a mixture of starch paste and animal glue) enzymatic hydrogels were used to remove the lining and adhesive residues. In particular, two Gellan gels loaded with different enzymes - *alpha-amylase* (*hydrolase*) and *Proteinase K* (*protease)* - were applied consecutively on the paper lining to help the hydrolysation of the strong and oxidized adhesive mix into soluble fragments inside the gels. By the combination of this biocompatible hydrogel and electrochemical sensors, we obtained a new tool for diagnostic and cleaning use, able to select and detect the enzymatic products during the treatment. In this way we can perform an on-line and continuous analysis, using all the instrumentation on site, avoiding also lengthy applications and waste of expensive products.

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THE COLOURS OF THE "COPTIC" TEXTILES AT THE *MUSEO EGIZIO DI TORINO*

M. Gulmini[1], A. Idone[1], P. Davit[1], E. Diana[1], F. Natale[1], F. Dal Bello[2], M. Borla[3], C. Greco[4] and M. Aceto[5]
[1]Dipartimento di Chimica, Università degli Studi di Torino, Via P. Giuria, 7 – 10125 Torino
[2]Dipartimento di Biotecnologie Molecolari e Scienze per la Salute, Università degli Studi di Torino, Via Nizza, 52 – 10125 Torino
[3]Soprintendenza Archeologia del Piemonte, Piazza S. Giovanni, 2 - 10122 Torino
[4] Museo Egizio di Torino, Via Accademia delle Scienze, 6 - 10123 Torino
[5]Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, Viale T. Michel, 11 - 15121 Alessandria & Centro Interdisciplinare per lo Studio e la Conservazione dei Beni Culturali (CenISCo), Università degli Studi del Piemonte Orientale, Via A. Manzoni, 8 - 13100 Vercelli

The "Coptic" textile collection of the *Museo Egizio di Torino* consists of about 250 textiles. Many of them are fragments of coloured decorations and the information relating to age and specific provenance is partially or totally missing. The whole collection has been subjected to a systematic multidisciplinary scientific investigation. Dyes were also investigated to complement the set of technological information available for each textile.
Various analytical approaches were employed in order to reach different levels of information on the dyes and on the dyeing techniques.
A preliminary non-invasive screening by fibre optics diffuse reflectance spectroscopy and portable fluorimetry was performed and enabled the clustering of the textiles according to red and purple dyes (dyes from scale insects, from madder root or from sea snails were employed).
High performance liquid chromatography coupled with diode array and mass spectrometric detectors was then employed for selected textiles to go deeper into the dyeing materials and enabled the detection of lac dye as the scale insect dye and of weld as the yellow colouring material.
The combined contribution of the non-invasive and micro-invasive analytical investigations revealed a peculiar dyeing procedure, where madder and lac dye were employed to obtain the final colour. Moreover, the whole set of analytical data was compared with dyeing materials found in other "Coptic" textiles dated with radiometric techniques, in order to possibly link the dyes with specific periods of production.
As a further aspect, a micro-invasive procedure by non-extractive surface enhanced Raman spectroscopy on silver colloidal pastes was set up on reference samples and then successfully applied for detecting weld in fibres sampled from the Coptic textiles.

CHARACTERIZATION OF CORROSION PRODUCTS OF ROMAN BRONZE COINS USING TRADITIONAL (SEM-EDS, XRD) AND ELECTROCHEMICAL (VMP, EIS) TECHNIQUES

F. Di Turo[a], N. Montoya[b], J. Piquero-Cilla[b], C. De Vito[a], R. Antiochia[c], F. Mazzei[c], G. Favero[c], A. Doménech-Carbó[b]
[a] Department of Earth Sciences, Sapienza University of Rome, P.le Aldo Moro 5, Rome, Italy
[b] Departament de Química Analítica. Universitat de València. Dr. Moliner, 50, 46100 Burjassot (València) Spain.
[c] Department of Chemistry and Drug Technologies, Sapienza University of Rome, P.le Aldo Moro 5, Rome, Italy

The conservation of bronze can be affected by several factors, such as temperature, humidity, acid rain, atmospheric particulate matter, sulphur oxides, nitrogen oxides and marine aerosol, and at least, burial condition that determine the formation of the patina. Numerous methodologies have been extensively applied in the study of ancient metal artefacts; investigation methods include Scanning Electron Microscopy (SEM-EDS), X-ray Diffraction (XRD), μ-Raman spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Laser Inductively Coupled Plasma (LA-ICP-AES) and other techniques. Unfortunately, among them some analytical techniques are micro-invasive, thus damaging the surface of the archaeological object and in the worst cases the analysis is destructive. In this context, solid state electrochemical techniques can provide a satisfying complement to other methodologies whose application on Cultural Heritage's field has been extended to a variety of materials. The Voltammetry of Microparticles (VMP), based on the record of voltammetric response of a solid micro- or nanosample mechanically transferred to the surface of an inert electrode immersed into an appropriate electrolyte, is particularly suitable for archaeometric analysis because of its high inherent sensitivity. Recently, Electrochemical Impedance Spectroscopy (EIS) was applied in studies of Cultural Heritage materials especially in evaluating coating treatments effectiveness but EIS demonstrated also to be suitable for the evaluation of deterioration and patina's formation because it can provide not only quantitative data but refers to corrosion processes and alteration products, too. In this work, the patina formed on archaeological Roman coins was characterized using both traditional (stereomicroscopy (SM), scanning electron microscope (SEM) and X-ray diffraction (XRD)) and the electrochemical techniques. In particular, VMP technique was applied in order to differentiate various class of coins, especially different for age or mint and it was complemented with EIS operating either in solution or using a Gel Polymer Electrochemical Cell (GPEC), the latter suitable for surface mapping of deterioration products.

CHARACTERIZATION OF BRASS ALLOYS AGED AT OPEN CIRCUIT POTENTIAL IN NEUTRAL SOLUTIONS BY XPS and XAES.

F. Cocco[1], B. Elsener[1,2], M. Fantauzzi[1], A. Rossi[1]
[1]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Campus di Monserrato S.S. 554 – Cagliari – Italy
[2]ETH Zurich, Institute for Building Materials, ETH Hönggerberg, CH-8093 Zurich

Contemporary musicians intend to play original instruments in concerts according to the "historically informed performance practice". The main concern of museums and conservators is corrosion of the brass instruments that might damage the artifacts on long-term. A small electrochemical sensor was used to assess corrosion potentials and corrosion rate on tuning slides of different brass instruments before and after being played and to check the effect of preventative measures (drying), but the surface state at the point of measurement in the tuning slides is not known.
This work intends to establish the relation between electrochemistry and surface state combining electrochemical tests (open circuit potential, linear polarization resistance and electrochemical impedance spectroscopy) and surface analytical techniques using the X-ray Photoelectron Spectroscopy (XPS/XAES). Model brass alloys with a zinc content between 18 and 37% were exposed up to 16 hours to solutions simulating the environment that could be present inside the brass wind instruments during and after playing: a diluted phosphate buffer solution (pH 7) and an artificial saliva solution. The surface state was characterized before and after the ageing tests by XPS/XAES. First an analytical method based on the CuLMM and ZnLMM signals to identify the chemical state of copper and zinc and to perform the quantitative analysis of thin-layered systems on brass was developed [1]. The results showed that corrosion rates were initially higher in the artificial saliva compared to the phosphate buffer solution. With prolonged exposure (ageing) to the artificial saliva the corrosion rate strongly decreased and a thick surface film composed of CuSCN and $Zn_3(PO_4)_2$ is formed. In phosphate buffer solution pH 7 only thin films mainly of Cu_2O, CuO and $Zn(OH)_2$ were detected. Thus the decrease of the corrosion rate with the immersion time of brass alloys in artificial saliva can be explained with the formation of a protective film on the surface. XPS/XAES and electrochemical experiments on laboratory samples with known surface state are ongoing in order to correlate the results of electrochemical measurements inside the historical instruments to the (not directly accessible) surface state.
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TECHNOLOGY AND PROVENANCE OF THE MAIOLICA SCULPTURES FROM OSTRA VETERE AND ANCONA (MARCHE, ITALY)

M. L. Amadori[1], P. Fermo[2]

[1]University of Urbino, Department of Pure and Applied Sciences
[2]University of Milan, Department of Chemistry

The majolica sculpture of the late XV and early XVI century is one of the most fascinating and problematic subjects of the study of Italian ceramic art. The majolica sculptures, object of this study whose origin is not documented, are linked to the area between Marche and Emilia Romagna, and can be placed chronologically at the end of the XV/ early XVI. In particular we have investigated two majolica reliefs from Ostra Vetere, one depicting the Nativity and the other the Lamentation with the emblem of the Montefeltro dukes of Urbino (fig. 1), and a relief from Ancona,

Fig.1 Nativity, Ostra Vetere

symbolizing the Lamentation. The sculptures were submitted to scientific investigations to acquire information on the composition, manufacturing and technology. Nine micro-samples, representative of the coatings and the ceramic body were collected and analyzed by optical microscope (MO) and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX). Furthermore the chemical composition has been investigated by atomic absorption spectroscopy (FAAS). The results show that all the artefacts were made with marly clay. The pastes are extremely fine and not very porous with a color related to the content in iron oxides (between 5 and 6%) and to the cooking in oxidizing atmosphere at temperatures probably around 950 ° C. The raw materials used for the relief from Ostra Vetere and Ancona show a good affinity with local clays and with a part of the Renaissance contemporary materials from Pesaro and Fano. As regards the glazes of Ostra Vetere, the thickness is irregular (maximum 140 μm) and an *ingobbio* is present in contact with the paste, probably made with fine white clay and quartz sand. The presence of this opaque slip and the lack of tin oxide are the indices of a technology similar to the "half majolica". In general the analysis on the glazes have shown the presence of antimony for the yellow, copper for the green, cobalt for the blue, manganese for the purple or the black and iron for the light or dark brown.

CHEMILUMINESCENCE LATERAL FLOW IMMUNOASSAY FOR A NEW GENERATION OF PORTABLE PAINT ANALYSIS KITS

G. Sciutto[1], M. Zangheri[2], F. Di Nardo[3], L. Anfossi[3], M. Mirasoli[2], S. Prati[1], M. Guardigli[2], C. Baggiani[3], R. Mazzeo[1], A. Roda[2]
[1] Microchemistry and Microscopy Art Diagnostic Laboratory Department of Chemistry "G. Ciamician", University of Bologna, Via Guaccimanni 42, 48121 Ravenna, Italy
[2] Department of Chemistry "Giacomo Ciamician", University of Bologna, Via Selmi 2, 40126, Bologna, Italy
[3] Department of Chemistry, University of Torino, Via Giuria 5, 10125 Torino, Italy

The ability to rapidly gain information on artistic materials and degradation products is fundamental to address conservation issues and restoration actions. Thus the application of analytical chemistry to conservation sciences is continuously evolving. On the other hand, long operating time and high costs connected with traditional laboratory analyses often hinder sustainable diagnostic campaigns. Thus, simple, rapid, portable and highly sensitive assays, suitable for point-of-use applications, represent a key alternative to establish a new role of chemical diagnosis in restoration.
To this aim, a new device for multiplexed analyses was developed by using a lateral flow immunoassay (LFIA) system ad hoc designed, which allows the simultaneous detection of two different proteins widely used in artistic samples: ovalbumin and collagen.
LFIA allows to perform rapid analysis with a user-friendly operation mode, exploiting the high selectivity of antigen-antibody binding. In particular, the assay is based on the use of a competitive immunochemical approach in combination with an enzyme-catalyzed chemiluminescence (CL) reaction for the detection of the antibody complexes, greatly simplifying the procedure and reducing the quantity of sample required (which is usually available in a very limited amount). Moreover, thanks to the use of a portable imaging device for CL signal measurement, based on a thermoelectrically cooled CCD camera, analysis can be performed directly on-field.
A miniaturized analytical device was also designed to assure a fast applicability by not specialized scientists, prompting the use of innovative portable analytical devices with enhanced sensitivity and multiplexed capabilities. Effective results obtained on several historical paint samples submitted to analysis validate the method for the characterization of real case studies.

EVALUATION OF THE TOXICOLOGICAL IMPACT OF TEXTILE INDUSTRY USING A MULTI-CRITERIA RANKING OF TOXIC COMPOUNDS

E. Gregoris[1,2], M. Roman[1,2], A. Gambaro[1,2], C. Barbante[1,2]
[1]Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari di Venezia, Via Torino, 155 – 30172 Venezia
[2]Istituto per la Dinamica dei Processi Ambientali, Consiglio Nazionale delle Ricerche (IDPA-CNR), Via Torino, 155 – 30172 Venezia

Conducting a global toxicological evaluation of chemicals is a considerable challenge, as each single chemical is characterised by specific toxicological features (lethal effects, carcinogenicity, etc.). Given the increasing concern regarding the use of chemicals in everyday life and workplaces, in recent years several methods for chemical hazard screening have been developed [1, 2]. In all cases, a limited number of categories was defined, thus significant difference in toxicity among chemicals could be minimised. In this work, a number of chemicals were subjected to a toxicological ranking based on the most important types of toxicity using multi-criteria analysis (MCA). Data about pollutant global hazard and concentration values in wastewater were combined to provide an indication about the toxicological impact of textile factories. GreenPeace identified eleven classes of hazardous chemicals that should be eliminated by top brands in the framework of the "Detox" campaign [3], with the aim of reducing water pollution caused by the textile industry. The MCA ranking included the above mentioned classes of chemicals with the addition of cyanide, given its known lethal effect. The types of toxicity selected as criteria were: acute toxicity, carcinogenicity, reproductive toxicity, acute aquatic toxicity and chronic aquatic toxicity, in this order of importance. Heavy metals and cyanide were the most dangerous compounds identified by the assessment. On average, the most polluting facilities were located in India and China. Since incoming water was usually characterised by a minimum toxicological impact, the responsibility for the high toxicity scores of facilities were assigned to the suppliers.

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PREPARATION OF NEW COMPOSITE MATERIALS FOR PHOSPHOPEPTIDE ENRICHMENT IN SHOTGUN PHOSPHOPROTEOMICS

A.L. Capriotti, F. Ferraris, S. Piovesana, A. Laganà
Dipartimento di Chimica - Università degli Studi di Roma "La Sapienza", Piazzale Aldo Moro, 5 – 00185 Rome, Italy

Protein phosphorylation is one of the most extensively studied post-translational modification due to critical role it plays within cells. However, phosphorylation mapping is still challenging, due to the low abundance of phosphoproteins and ion suppression during mass spectrometry analysis. In this context, enrichment prior to analysis is fundamental [1], but currently no system is able to provide a comprehensive coverage of the phospohoproteome in complex systems [2].
Thus, the aim of our research was to develop new materials based on affinity chromatography for the highly selective enrichment of phosphopeptides. The selected approach relied on the magnetic solid phase extraction, due to its ease of use with respect to conventional packed miniaturized columns and versatility, since it applicable to both small and large scale experiments without need of employing multiple parallel spin-columns.
In one case, bare Fe_3O_4 magnetic nanoparticles were covered with polydopamine, a biocompatible polymer easily produced by the spontaneous polymerization of dopamine under basic conditions in order immobilize Ti^{4+} cations on the surface of the nanoparticles. An optimized protocol was developed and tested on standard protein digests and commercial cow milk, with good results compared to a standard commercial enrichment kit.
In the second case, new composite magnetic phases were prepared exploiting affinity chromatography to TiO_2. Carbon materials, starting from graphitized carbon black (GCB), were employed to produce hybrid magnetic materials which coupled the large surface area of carbon materials with the selectivity for phosphopeptides by TiO_2. This new phase was first tested on the standard mix and then optimized on a more complex yeast extract. Different sample to phase ratios were tested to maximize the selectivity of the protocol.
All enrichment methods were developed embedding the protocol in a typical shotgun proteomics workflow, comprising nanoHPLC, high resolution mass spectrometry and bioinformatics data analysis, for performance evaluation and comparison to established methods.

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SOIL METAPROTEOMICS: LC/HRMS-BASED ANALYTICAL STRATEGY FOR THE STUDY OF MICROBIAL FUNCTIONS IN THE RHIZOSPHERE OF PLANTS FROM SERPENTINE SOIL

M. Mattarozzi[1], M. Manfredi[2], B. Montanini[3], F. Gosetti[2], A.M. Sanangelantoni[3], E. Marengo[2], G. Visioli[3], M. Careri[1]
[1]Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze, 17/A – 43124 Parma
[2]Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, Viale Teresa Michel, 11 – 15121 Alessandria
[3]Dipartimento di Bioscienze, Università degli Studi di Parma, Parco Area delle Scienze, 11/A – 43124 Parma

Metaproteomics seeks to extensively characterize the protein complement expressed by the whole microbial community in an environmental sample. However, the development of analytical strategies for soil metaproteomics is still a very challenging issue due to microbial diversity, soil matrix complexity as well as limited metagenomic information [1].
In a research program dealing with mass spectrometry (MS)-based bottom-up proteomic investigation [2], in this study a shotgun proteomic strategy, involving liquid chromatography-high resolution MS analysis of tryptic peptides, was followed to map the major bacterial functions associated with the rhizosphere of metal tolerant and metal hyperaccumulator plants, growing in a stressful serpentine soil naturally contaminated by heavy metals, such as Ni, Co, Cr. To obtain the highest representation of soil bacterial functions, we previously carried out metagenomic investigation to build an "in-house" bacterial protein database, based on the results of 16S rDNA profiling, which was used for protein identification. In addition, to achieve a higher coverage of the total protein content from the soil samples and minimize the risk of taxonomic and functional bias, we combined the information from three different protocols for direct cell lysis and protein extraction from soil. Almost 800 proteins were identified, corresponding to functions assigned to proper Gene Ontology categories. Mainly proteins involved in response to stimulus or in transport of metals and nutrients revealed variability of bacteria responses to microenvironment conditions. As for taxonomy, five bacterial species showed to be more represented in the rhizosphere samples of the metal tolerant *Biscutella laevigata* and of the Ni hyperaccumulator *Noccaea caerulescens* respect to bulk soil.

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EVALUATION OF OBETICHOLIC ACID PHARMACOKINETICS, BIODISTRIBUTION AND METABOLISM IN DECOMPENSATED LIVER CIRRHOTIC RATS BY HPLC-ESI-MS/MS.

A. Roda[1], R. Aldini[2], P. Franco[1], M. Cont[3], L. Maroni[4], L. Adorini[5]
[1]Dipartimento di Chimica, Università di Bologna, Via Selmi, 2 – 40126 Bologna
[2]Dipartimento di Farmacia e Biotecnologie, Università di Bologna, Via Belmeloro, 6 – 40126 Bologna
[2]INBB, Istituto Nazionale Biostrutture e Biosistemi, Roma, Viale delle Medaglie d'Oro, 305 - 00136 Roma
[4]Dipartimento DIMES, Università di Bologna, Via Massarenti, 9 – 40128 Bologna
[5]Intercept Pharmaceuticals, 450 W 15th Street, Suite 505 - 10011 New York

Obeticholic Acid (OCA) is a semisynthetic bile acid (BA) analogue and potent FXR agonist. It is the analogue of chenodeoxycholic acid (CDCA), with an ethyl group in the 6α-position that confers to OCA its potent FXR agonistic activity [1]. OCA is under medical investigation as drug for the treatment of hepatic pathologies, such as Primary Biliary Cirrhosis [2] and Nonalcoholic Steatohepatitis [3]. Considering its current use in clinical practice, it is important to evaluate OCA pharmacokinetics and metabolism in a model of liver disease to determine potential undesirable localization in specific organs or biological fluids, especially when chronically administered. With this aim an HPLC-ES-MS/MS method was developed [4] to quantify endogenous BA, OCA and its main metabolites in plasma, liver, stools, intestinal contents, urine and kidneys samples. The developed method proved to be accurate (bias%<15%), precise (CV%<12%) and with an high detectability (LOQ<10 nM); matrix effects doesn't significantly affect the analysis accuracy and determined recoveries are higher than 85%. The use of the MRM detection mode ensures high sensitivity and the possibility to discriminate different structural isomers in order to obtain a complete metabolomic profile, including minor metabolites as glucoronides and sulphates. The method was successfully applied to a study of OCA pharmacokinetics and metabolism in a rat model of induced decompensated liver cirrhosis by CCl_4 inhalation for 13 weeks. OCA hepatic metabolism and biliary secretion were also studied in cirrhotic rats using the bile fistula model after intravenous administration. Results showed that OCA plasma concentrations were not at risk of producing unsafe levels in specific organs.

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MULTICOLOURS GOLD NANOPARTICLES FOR IMMUNOCHROMATOGRAPHIC STRIP TEST

F. Di Nardo[1], L. Anfossi[1], C. Giovannoli[1], G. Spano[1], C. Baggiani[1]
[1]Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria, 5 – 10125 Torino

During the last decades, noble metal nanoparticles (NPs) have increased the breadth of their impact and are now becoming a backbone of modern technology. Their applications range from biomedical, electronics, catalysis, sensing of organic and biomolecules, to optical devices and many others [1]. Gold nanoparticles (AuNPs) are one of the most used NPs [2]. Due to the strong surface plasmon resonance, AuNPs can be used as sensitive probes for colorimetric sensors. Colorimetric assay based in AuNPs are acquiring increasing attention thanks to the advantages of simplicity, rapidity, cost-effectiveness and no requirement of any sophisticated instrumentation.
The immunochromatographic strip test (ICST) is one of the most successful colorimetric assay; it is based on the specific interaction between antibodies and antigens and the use of AuNPs as antibodies label allow a naked-eye detectability. The typical AuNPs used in ICST are mainly spherical, with a diameter of 30 nm, and their sols exhibit a deep-red colour, which reflects the surface plasmon resonance (SPR) band, an absorption band in the visible region around 525 nm. The size and shape of AuNPs have significant influences on the SPR band, optical and colloidal properties, and therefore are critical for ICST stability and sensitivity.
We synthesised highly complex flower-like AuNPs through a seeding growth approach. The UV-vis spectra demonstrate that the SPR band of prepared gold nanoflowers (AuNFs) exhibit the maximum absorption at around 620 nm, which is consistent with the blue colour observed.
Recently, Ji *et al.* tried to use similar AuNFs in ICST, reporting higher optical brightness and better colloidal stability than conventional AuNPs [3]. On the basis of these information, we focused our attention on the study of AuNFs stability, characterization (performed using a transmission electron microscope), synthesis and on the comparison with AuNPs.
The results of our study will be discussed in this communication, along with the development of a duplex-ICST using multicolour gold nanoparticles to detect two mycotoxins in maize flour.

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BINDING PROPERTIES OF ENZYME TRACERS TO MOLECULARLY IMPRINTED POLYMERS AS MIMICS OF ANTIBODIES

C. Baggiani, G. Spano, C. Giovannoli, F. Di Nardo, L. Anfossi
Dipartimento di Chimica, Università degli Studi di Torino, Via Giuria, 5 – 10125 Torino

Molecularly imprinted materials are often described as a sort of artificial antibodies which share with natural antibodies the same binding behaviour. It is therefore not surprising that many have thought of using them as artificial receptors in the so-called "molecularly imprinted sorbent assay".[1] Despite the feasibility of such assays has been shown, and their potential efficacy has been demonstrated in many studies, with respect to other fields of application typical of molecular imprinting technology, molecularly imprinted sorbent assay is still in a developmental stage of proof-of-principle, and a certain number of relevant issues remain to be solved.
One of the most relevant issues concerns the generalized use of enzyme-labelled templates as traces in ELISA-like assays. In fact, unlike the binding sites of antibodies that are easily accessible and exhibit antigen induced fit, imprinted materials show narrow porosity and rigidity of the polymer structure. This implies problems of steric hindrance at the entrance of the ligand in the binding sites. As a consequence, binding kinetics can be slow and unfavourable to the development of an assay. More drawbacks are present when the ligand is covalently conjugated to an enzyme tracer. In fact, imprinted materials work well in organic or mixed aqueous/organic solutions but enzymes are sensible to inactivation in such media. Moreover, enzymes are biomacromolecules characterized by slow diffusion in nanometer-sized pores typical of imprinted materials, making impractically slow the assay kinetics. Last but not least, imprinted materials have moderately hydrophobic surfaces, prone to irreversibly adsorb biomacromolecules like enzymes, thus increasing the analytical signal due to non-specific interactions.
To study the binding behaviour of template-enzyme conjugates towards imprinted materials we prepared two types of cortisol-imprinted polymers: (i) imprinted layers grafted onto glass surfaces, and (ii) sub-micron imprinted particles adsorbed onto microtitration plates. The adsorption of unconjugated or cortisol-conjugated horseradish peroxidase was studied, evaluating the effect of the different experimental conditions on the binding of the enzyme, with the ultimate goals to maximize the tracer selective binding and minimize the non-selective binding by the imprinted surfaces.

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ELEMENTAL CONTENT IN HUMAN PLACENTA: THE EFFECT OF GESTATIONAL DIABETES MELLITUS AND OF OTHER FACTORS

M. Roverso,[1,2] F. Lorigiola[1], V. Di Marco[1], D. Badocco[1], P. Pastore[1], S. Visentin[3]
[1]Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1 – 35131 Padova
[2]Dipartimento di Medicina, Università di Padova, via Giustiniani 2 – 35128 Padova
[3]Dipartimento di Salute della Donna e del Bambino, Università di Padova, via Giustiniani 2 – 35128 Padova

The knowledge of the metallomics of Gestational Diabetes Mellitus (GDM) is an important task in order to gain information about the molecular causes of this disease. In our previous work [1], the elemental content of several placentas was determined, and some key elements were identified to be statistically different among healthy women and controls. In this work, other placentas were analyzed, and several changes in the procedure and in the data analysis were introduced. The analytical method was refined and optimized to obtain more reliable results. More sampling points in each placenta were considered for the study, in order to evidence possible zone-related differences in the elemental content. Additional factors were considered to better understand the previously observed correlations and to interpret the experimental results. In particular, the mother age, weight, and etnicity, were added in the subsequent statistical tests and principal component analysis of the whole data set. Several of the considered factors appear to significantly affect the elemental content results, thus allowing to discriminate in a more reliable way the metallomic effect of the GDM pathology on placentas.

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THE EFFECT OF EXERCISE ON SALIVARY LACTATE, ALPHA-AMYLASE AND URIC ACID IN HEALTHY VOLUNTEERS

T. Lomonaco[1], S. Ghimenti[1], E. Bramanti[2], D. Biagini[1], F. G. Bellagambi[1], M. Onor[2], R. Fuoco[1], F. Di Fancesco[1]
[1]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa, Via Giuseppe Moruzzi, 13 – 56124 Pisa
[2]Istituto di Chimica dei Composti Organometallici, Consiglio Nazionale delle Ricerche, Via Giuseppe Moruzzi, 1 – 56124 Pisa

Monitoring the training load of an athlete is an important aspect to improve their performance as well as to minimize the risk of non-functional overreaching, injury, and illness. To date, several external (e.g. time-motion analysis) and internal (e.g. blood lactate) parameters are currently used to monitor the effectiveness of a specific training load. The main drawbacks of biochemical analyses, required for monitoring specific biomarkers, are the need to collect venous blood samples, making this approach uncomfortable for many athletes. The use of oral fluid in the monitoring of athletes is an attractive approach because this technique is less invasive and unsafe. As a consequence, oral fluid samples may be collected several time from one subject, allowing a sort of real-time monitoring during and after physical tests, training or competitions. Nevertheless, taking into the account the analyte to be quantified, oral fluid analysis requires a standardization of the collection procedures in order to compare data from different coaches and supporting staff.
The aims of this work was to i) evaluate the influence of sampling procedures on the quantification of alpha-amylase, lactate and uric acid in oral fluid samples and ii) determine if the analysis of these biomarkers can be used as an alternative indicator of the exercise intensity. For this purpose, ten healthy volunteers (5 females and 5 male) underwent incremental exercise on a cycle ergometer, at constant 70 rpm, with increment of about 20 W every three minutes until voluntary exhaustion or impossibility to maintain current workload. Stimulated oral fluid samples were collected 5 minutes before the exercise, every 3 minutes during workload and 10, 30 and 40 minutes after the end of the test. Peripheral capillary oxygen saturation (SpO_2) and heart rate values were continuously monitored during all the entire experiment. The concentrations of lactate and uric acid are influenced by the flow rate, since these two compounds do not diffuse through the salivary membrane due to their low hydrophobicity. Pearson's correlation highlighted a good relationship ($r = 0.6$, $p < 0.01$) between heart rate and alpha-amylase activity in oral fluid. Lactate and uric acid levels increased during the exercise as a consequence of the increase of work load, whereas a sharp decrease, approaching baseline values, of these two compounds was observed in the recovery phase.

PRENATAL SCREENING USING MS-BASED PROTEOMIC APPROACH ON COELOMIC FLUID: A PILOT STUDY

D. Aiello[1], F. Mazzotti[1], A. Giambona[2], F. Leto[2], C. Passarello[2], G. Damiani[3], V. Cigna[3], G. Schillaci[3], A. Maggio[2], A. Napoli[1]
[1]Department of Chemistry and Chemical Technologies, University of Calabria, Ponte Bucci – 87036 Arcavacata di Rende (CS)
[2]Unit of Haematology for rare diseases of blood and blood-forming organs, Regional Reference Laboratory for screening and prenatal diagnosis of hemoglobinopathies, Palermo
[3]Unit of Prenatal Diagnosis, Hospital Villa Sofia Cervello, Palermo

Coelomic cavity fluid (CF) is the earliest fluid of the gestational sac amenable to prenatal screening and it is used for the morphological analyses of fetal cellular component and cell-free DNA. Coelocentesis is the selectively aspiration of CF under ultrasound guidance using a transvaginal route as of 7 weeks of gestation. Coelocentesis represent the ideal technique for very early prenatal diagnosis, since it shorten the time to diagnosis by at least 1 month respect chorionic villous sampling, exclude the risk of placental vascular damage and its associated risk of fetal abnormalities and it would make in utero stem-cell therapy possible before the fetus becomes immunologically competent. CF is a dynamic and complex mixture that reflects the physiological status of the developing fetus and became an interesting biological fluid for a proteomic approach. In the present study human coelomic fluid (CF) from pregnancies with chromosomally normal fetuses in the 8th week of gestation were analyzed by iTRAQ LC-MALDI MS/MS analysis. An MS-compatible depletion step prior to proteomic analysis was planned to remove most abundant proteins of maternal origin (albumin, IgG, IgA, transferrin, haptoglobin and α1-antitrypsin) and to improve the detection sensitivity of fetal low-abundant proteins. In order to perform the quantitative study, the comparison was be done between a pool of nine CF samples and three individual samples. Using this approach 88 proteins were found differentially expressed. Furthermore, the CF proteome characterization allowed a direct identification and quantification of deregulated proteins/enzymes involved in central nervous system development, in neuronal differentiation and in fetal growth. This novel findings lead for the first time to a deeper understanding of the CF from a molecular perspective and can be a significant start point to plan new preborn screening methodologies and novel therapy.

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DETERMINATION OF BIOMARKERS IN BREATH AND SALIVA FOR MONITORING HEART FAILURE PATIENTS

F.G. Bellagambi[1], T. Lomonaco[1], S. Ghimenti[1], F. Di Francesco[1], M. Marzilli[2], R. Fuoco[1]
[1]Dipartimento di Chimica, Università di Pisa, Via Giuseppe Moruzzi, 13 – 56124 Pisa
[2] Dipartimento di Patologia Chirurgica, Medica, Molecolare e dell'Area Critica, Università di Pisa, Via Savi, 10 – 56126 Pisa

Heart failure (HF) is a complex clinical syndrome caused by a wide range of cardiovascular disorders, such as structural or functional abnormalities of the heart. The clinical status of a HF patient can be evaluated by detecting specific biomarkers of pathogenic biological processes. Beside conventional clinical investigations, breath and saliva analysis have been recognized as one of the most effective, easy, painless and non-invasive ways of identifying physiological and pathophysiological conditions.
This study was focused on the development and validation of analytical methods based on GC-MS/MS, HPLC-MS/MS, spectrophotometric and immunochemical techniques to determine specific breath and saliva biomarkers. Brain natriuretic peptides, 8-iso-prostaglandin $F_{2\alpha}$, uric acid, tumor necrosis factor-α, interleukin-10, aldosterone, α-amylase, lactate and cortisol in saliva samples, and acetone and isoprene in breath samples were determined. Special attention was paid to the optimization of the sampling procedures and sample handling.

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MIGRATION TESTS ON MODEL ANTIBACTERIAL Ag NPs COATINGS

D. Spanu[1], S.Recchia[1], D.Monticelli[1]
[1]Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Via Valleggio 11 – 22100 Como

Nanoparticles migration into foods from active packagings has a great concern with regards to taste modifications and potential toxicity. The assessment of migration extent and mechanism is therefore of primary importance. The utilisation of silver nanoparticles (Ag NPs) is continuously growing due to their well known antibacterial properties.
In this communication we would like to present the results of migration test carried out on model Ag NPs/PET films. The model film was prepared by a chemical vapour synthesis assisted by plasma in order to produce nanoparticles with variable dimensions.
.Ag NPs superficial distribution on PET was determined by laser ablation-inductively coupled plasma-mass spectroscopy (LA-ICP-MS), while total Ag concentration was determined by inductively coupled plasma-mass spectroscopy (ICP-MS) after acid microwave digestion.
Migration tests has been performed using typical food matrix like water, 3% acetic acid solution, hydroalcoholic solution (20-30% of alchol) and vegetable oil. The total Ag migrant levels in the food simulants were quantified by ICP-MS. Electron microscopy was used to characterise the nature of the released particles.
Preliminary results of uncommon migration tests conducted by direct contact with solid food will be also presented.

IN-FLIGHT MONITORING SALIVARY STRESS BIOMARKERS ON THE INTERNATIONAL SPACE STATION USING AN ULTRASENSITIVE MICROFLUIDIC-ASSISTED CHEMILUMINESCENT LATERAL FLOW IMMUNOASSAY

M. Zangheri[1], M. Mirasoli[1], M. Guardigli[1], L. Anfossi[2], F. Di Nardo[2], C. Giovannoli[2], C. Baggiani[2], P. Simoni[3], A. Roda[1]
[1]Dipartimento di Chimica "Giacomo Ciamician", Alma Mater Studiorum - Università di Bologna, Via Selmi 2-40126 Bologna
[2]Dipartimento di Chimica, Università di Torino, Via Giuria 5 – 10125 Torino
[3]Dipartimento di Medicina e Chirurgia, Alma Mater Studiorum - Università di Bologna, Via Massarenti 9 – 40138 Bologna

In the last years, Lateral Flow Immunoassays (LFIAs) have gained wide popularity and commercial success among the methods used for Point-of-Care (POC) applications, owing such achievements to the simplicity and rapidity of assay execution, as well as compactness, low cost and ease of use. While conventional LFIAs are available mostly for qualitative analyses, the use of enzymes as tracers, coupled with chemiluminescence (CL) detection, provides quantitative information and high detectability [1-2].
Analyses performed on biological fluids of astronauts during space missions for scientific or diagnostic purposes are currently performed on Earth, upon ground shipment of biosamples form the International Space Station (ISS). Nevertheless, this scenario is not feasible in long-term space missions, as future manned missions to Mars. Thus, POC analytical devices that can be safely and easily employed by the astronauts on-board ISS are required.
Here we report the development of an analytical device based on CL-LFIA that was developed for performing clinical analysis of saliva samples on the ISS, thus enabling crew members to non-invasively check their health status in real time. The device consisted of three elements: the equipment for saliva sampling, a microfluidic disposable cartridge containing reagents necessary for the immunoassay, an ultrasensitive CL reader equipped with a cooled CCD camera. The project focuses on determining the level of salivary cortisol, which is a biomarker of stress and appetite regulation. Data acquired by the astronaut will then be sent to Earth via telemedicine, allowing early detection of potential problems and the activation of the appropriate treatments.

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PROTEOMIC STUDY OF INDONESIAN WILD SILK COCOON OF *CRICULA TRIFENESTRATA* AND *BOMBYX MORI*

A.L. Capriotti, F. Ferraris, A. Laganà, S. Piovesana
Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza"

The development of functional materials that can interact with biological systems is nowadays of great interest. Such materials can be derived directly from nature or synthesized in the laboratory. However, despite the remarkable potential of man-made synthetics, their applications have been limited by challenges including biocompatibility, biodegradability and bioresorbability. The intrinsic advantages of natural materials lead to focus the research on silks, members of fibrous proteins family, with impressive mechanical strength, excellent biocompatibility, absence of immunogenicity, limited bacterial adhesion and controllable biodegradability.
Wild silks, not obtained from domesticated species, are primarily composed of proteins associated with certain macromolecules such as polysaccharides and lipids. The two primary proteins that comprise silk-cocoon silk are fibroin and sericin, consisting of 18 different amino acids: predominantly glycine, alanine and serine [1]. The amino acid sequences of silk proteins can vary from species to species, resulting in a wide range of mechanical properties [2].
This research is focused on wild silk cocoon of *Bombyx Mori* and *Cricula Trifenestrata* (no proteomic study has been done before on the latter) obtained from Indonesian source, and comprises a comparative proteomic analysis between the two cocoons and a final shotgun proteomic approach on the post translational modifications. In order to study these modifications, an upstream step of enrichment is required: for the specific enrichment of phosphopeptides, newly methods and stationary phases will be tested, i.e. coprecipitation methods [3] or spin columns with phosphate- specific-binding stationary phases [4].

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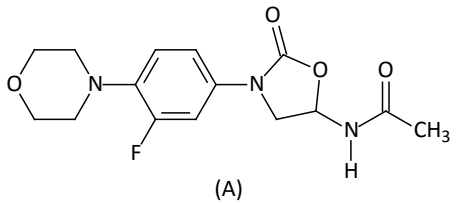
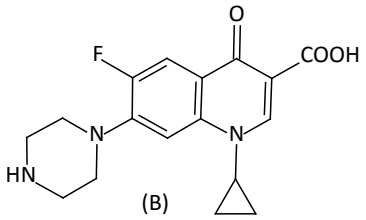
A BIOANALYTICAL MEPS-UHPLC-PDA METHOD FOR THE SIMULTANEOUS DETERMINATION OF LINEZOLID AND CIPROFLOXACIN IN HUMAN PLASMA OF HOSPITAL ACQUIRED PNEUMONIA PATIENTS

V. Ferrone[1], L. Di Marco[1], S. Genovese[1], R. Cotellese[2], M. Carlucci[2], P. Raimondi[2], G. Carlucci[1]
[1]Dipartimento di Farmacia, [2]Dipartimento di Scienze Mediche Orali e Biotecnologiche - Università degli Studi "*G. d'Annunzio*" Chieti-Pescara, via dei Vestini 31 – 66100 Chieti

Pneumonia is a respiratory infection of the lung affecting primarily the microscopic air sacs known as alveoli, it is defined as being nosocomial or hospital acquired (HAP) if it becomes apparent more than 48 h after hospital admission. HAP affects 0.5 to 1.0% of in patients and is the most common healthcare-associated infection contributing to death. The combination of two or more synergistic antimicrobial drugs provide a broad-spectrum coverage, prevent the emergence of resistant mutants and obtain a synergy between both antimicrobial agents [1].



(A)



(B)

An ultra high-performance liquid chromatographic (UHPLC) method with PDA detection was developed and validated for the simultaneous quantification of linezolid (A) and ciprofloxacin (B) in human plasma and applied in hospital acquired pneumonia to patients (HAP). The method uses a semi-automated microextraction by packed sorbent (MEPS) for sample preparation. Chromatography was carried out using a Waters BEH (50 x 2.1 mm i.d. , 1.7 μm) column and a gradient elution. Ulifloxacin was used as internal standard. The method showed good linearity with correlation coefficients (r^2) > 0.9994 for the two drugs, as well as high precision (RSD%) < 6% in each case) and accuracy (96.4-97.6%). The limit of quantification of the two drugs was established at 0.02 μg/mL. Linezolid, ciprofloxacin and internal standard, were extracted from human plasma with a mean recovery of 95%, 89.5% and 94.7%, respectively. This method will be subsequently used to quantify the drugs in patients with HAP to establish if the dosage regimen given is sufficient to eradicate the infection at the target site.

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NEW ANALYTICAL SOLUTIONS FOR PHARMACEUTICAL NANO/BIOTECHNOLOGY

B. Roda[1,2], A. Zattoni[1,2], V. Marassi[1], S. Casolari[1], P. Reschiglian[1,2]
[1]Department of Chemistry, University of Bologna, Via Selmi 2, 40126 Bologna, Italy.
[2]byFlow srl, Via Caduti della Via Fani 11/b, 40127 Bologna, Italy

The rapid development of protein-based and nanostructured pharmaceuticals highlights the need for robust analytical methods to ensure their quality and stability. Between proteins, used in pharmaceutical applications an important and ever increasing role is represented by monoclonal antibodies and large proteins, often modified to enhance their activity or stability when used as drugs. Functionalized nanoparticles are used as active compounds for delivery in pharmaceutical field. The bioactivity and the stability of those proteins and particles are closely related to morphology and the maintenance of their complex structure, however, influenced from many external factors that can cause degradation and/or aggregation. The presence of aggregates in these drugs could reduce its bioactivity and bioavailability and induce immunogenicity. The choice of the proper analytical method for the analysis of aggregates is fundamental to understand their (size) dimensional range; their amount and if they are present in the sample as generated by an aggregation or are an artifact due to the method itself. Size exclusion chromatography is one of the most important techniques for the quality control of pharmaceutical particles, however its application is limited to relatively low molar masses aggregates. Among the techniques for the size-characterization of proteins, field-flow fractionation (FFF) represents a competitive choice since its soft mechanism due to the absence of a stationary phase and the higher dimensional range of applications form nanometer to micrometersized analytes. The microcolum variant of FFF, the hollow-fiber flow FFF (HF5), is on-line coupled with multi-angle light scattering (MALS) for the development of methods for the characterization of protein based drugs [1,2]. The HF5-MALS was shown able to size-separate therapeutic protein samples and their aggregates and to evaluate the nature of aggregates. The analytical performances, such as resolution, reproducibility and limit of detection, were also determined in the framework of quality control of particles-based drugs.

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BEWARE OF UNRELIABLE Q^2! A COMPARATIVE STUDY OF REGRESSION METRICS FOR PREDICTIVITY ASSESSMENT OF QSAR MODELS

R. Todeschini, D. Ballabio and F. Grisoni
Milano Chemometrics and QSAR Research Group, Department of Earth and Environmental Sciences, University of Milano-Bicocca, P.za della Scienza, 1 – 20126 Milan (Italy)

Validation is an essential step of QSAR modelling and it is usually performed with an external set of test molecules, that is, chemicals not used for model development and/or optimisation. The evaluation of model predictive ability is then established comparing experimental and predicted values of test molecules. When dealing with quantitative QSAR models, validation results are generally expressed in terms of Q^2 metrics.
In this presentation, four fundamental mathematical principles, which should be respected by any Q^2 metric, are introduced. Then, the behaviour of five different metrics (Q^2_{F1}, Q^2_{F2}, Q^2_{F3}, Q^2_{CCC} and Q^2_{Rm}) is compared and critically discussed. The conclusions highlight that only Q^2_{F3} metric satisfies all the stated conditions, while the remaining metrics show different theoretical flaws.

COLOURGRAMS-GUI: A GRAPHICAL USER INTERFACE FOR EXTRACTING USEFUL INFORMATION FROM RGB IMAGES

R. Calvini, G. Orlandi, G. Foca, A. Ulrici
Dipartimento di Scienze della Vita, Università di Modena e Reggio Emilia, Pad. Besta – Via Amendola 2 – 42122 Reggio Emilia

Colour is an important property of food products, since colour-related attributes have a relevant role in quality assessment and in the decision of consumers. Therefore, the identification of fast and objective methods able to quantify visual aspects, or to codify some characteristics like amount and distribution of the colour is a key issue. To this purpose, analytical measurement systems can be easily implemented using common digital cameras, smartphones or flatbed scanners for the automated evaluation of colour-related parameters of food products. In this manner, the visual aspect of a food sample can be converted in a RGB digital image with fast and inexpensive methods.
The key point is then to extract the relevant information from such data, especially when dealing with large datasets of digital images. To this aim, a method has been developed by some of us based on the conversion of each RGB image into a one-dimensional signal, named *colourgram,* which codifies the overall colour-related content of the image [1, 2, 3]. In practice, colourgrams are obtained by merging in sequence the frequency distribution curves of a series of colour parameters extracted from the original digital images, like e.g. red, green, blue, hue, saturation, intensity and scores obtained from Principal Component Analysis on the unfolded image data. Therefore, a dataset composed by RGB images can be compressed into a matrix of colourgrams, which in turn can be analysed using multivariate statistical methods. For example, the colourgrams matrix can be simply investigated by calculating a PCA model to identify clusters of images or to evaluate trends.
In order to further facilitate the exploration of datasets of digital images, a Graphical User Interface (GUI) has been implemented in MATLAB environment. Colourgrams-GUI allows to easily calculate the signals, assign the samples to given categories, explore the dataset by PCA and visualize features of interest in the original image domain.

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STRATEGIES FOR NON-LINEAR MODELING

F. Marini
Dipartimento di Chimica, Università di Roma "La Sapienza", P.le Aldo Moro 5 – 00185 Roma

Modern analytical chemistry is evolving towards the use of more and more comprehensive and high throughput fingerprinting techniques, at the same time looking for the minimum sample pretreatment. This issues results in the analytical signals being affected by different sources of variability which, in turn, reflects in the relationships between the recorded profiles and the properties to be predicted not to be linear anymore.
From the data analytical standpoint, non-linear relationships require non.linear chemometric approaches to be modeled accurately. In this respect, many different methods are available, differing in the extent in non-linearity, in the requirements in terms of samples to variable ratio and also in their tendency towards overfitting.
In the present communication, attention will be focused on the family of methods based on the concept of local modeling, i.e. on the idea that a mathematical relationship that is globally non-linear may be approximated by piecewise linear functions. In particular, the characteristics of locally weighted PLS for calibration and classification will be described and particular attention will be focused on discussing the interpretation of the local models obtained.
Moreover, a recent generalization to multi-way arrays providing very accurate regression and classification models for data coming from hyphenated techniques will also be presented.

EVALUATION OF DIRECT ALCOHOL BIOMARKERS USING MULTIVARIATE AND LIKELIHOOD RATIO APPROACHES TO IDENTIFY CHRONIC ABUSERS FOR FORENSIC PURPOSES

E. Alladio[1,2], A. Martyna[3,4], A. Salomone[2], V. Pirro[5], M. Vincenti[1,2], G. Zadora[4,6]
[1]Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 7, 10125 Torino, Italy.
[2]Centro Regionale Antidoping e di Tossicologia "A. Bertinaria", Regione Gonzole 10/1, 10043 Orbassano, Torino, Italy.
[3]Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland
[4]Institute of Forensic Research, Westerplatte 9, 31-033 Krakow, Poland.
[5]Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, 47907 Indiana, USA.
[6]Department of Analytical Chemistry, Chemometric Research Group, The University of Silesia, Szkolna 9, 40-006 Katowice, Poland.

The determination of direct ethanol metabolites – such as ethyl glucuronide (EtG) and fatty acid ethyl esters (FAEEs) – to be quantified in the keratin matrix is currently regarded as the optimal strategy to effectively recognize chronic alcohol misuse conditions [1]. Even if cut-off values have been established by the Society of Hair Testing to interpret EtG and FAEEs results as a dichotomic choice (positive vs. negative), several environmental and behavioural factors (e.g. cosmetic treatments) may strongly affect their actual hair concentrations, resulting in a biased outcome with respect to the real alcohol intake and the inherent evaluation process. Multivariate Data Analysis (e.g. Partial Least Squares – Discriminant Analysis; PLS-DA) and multivariate likelihood ratio (LR) models were investigated to overcome the drawbacks of the traditional approach based on cut-off values and dichotomic interpretation. Several multivariate models were evaluated and their effectiveness in discriminating chronic alcohol misusers from non-chronic alcohol consumers was examined. Successful results were observed with both LR and PLS-DA models, showing correct classification rates close to 100%. The systematic use of a multivariate LR approach is proposed as an efficient way to corroborate the diagnosis of chronic abuse, since it provides knowledge about the strength of classification criteria (i.e., strong vs. weak evidence) and a quantitative scale to support the selected proposition, making doubtful classifications worth of further in-depth analysis.

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DIRECT ELECTRODEPOSITION OF GOLD NANOPARTICLES ONTO GLASSY CARBON ELECTRODE AS BIOFUEL CELL BIOANODE BASED ON CELLOBIOSE DEHYDROGENASE

P. Bollella[1], R. Ludwig[3], G. Favero[1], F. Mazzei[1], Lo Gorton[2], R. Antiochia[1]
[1]Department of Chemistry and Drug Technologies, Sapienza University of Rome P.le Aldo Moro 5, 00185 – Rome, Italy
[2]Department of Analytical Chemistry/Biochemistry, P.O. Box 124, 221 00 – Lund, Sweden
[3]Department of Food Sciences and Technology, Food Biotechnology Laboratory, BOKU–University of Natural Resources and Life Sciences, A-1190 Vienna, Austria

In the last decades, nanomaterials have shown great advantages in terms of functional properties for a wide range of technological applications [1]. Metal nanoparticles provide a lot of advantages compared to macroelectrodes, such as enhancement of mass transport, catalysis, high effective surface area and control on the electrode conductive microenvironment. Gold nanoparticles (AuNPs) can be synthesized by using a chemical approach and electrodeposition. The main advantages of the electrodeposition method are the thickness, roughness and size control of the AuNPs layer [2].
In this work AuNPs were directly electrodeposited onto a glassy carbon electrode (GCE) by sweeping the potential from in an acidic solution of $HAuCl_4$ which acted as gold precursor [3]. In a first step we optimized the different parameters that can affect the electrodeposition process, such as scan numbers, concentration of precursor solution, etc. Afterwards the nanostructured electrodes morphology was studied by using scanning electron microscopy (SEM). The electrochemical characteristics of the modified electrodes were characterized in $Fe(CN)_6^{3-/4-}$ by using cyclic voltammetry and electrochemical impedance spectroscopy, and compared to the naked GCE and the naked gold electrode (AuE), in order to determine the electroactive area (A_{EA}), electron transfer rate constant (k^0) and the roughness factor (ρ).
Finally, the so modified electrode was used with cellobiose dehydrogenase from *Corynascus thermophilus* [4] to realize a biofuel cell bioanode suitable to work at human blood conditions [5].

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DEPOSITION AND CHARACTERIZATION OF A COBALT HEXACYANOFERRATE NANOROD ARRAY IN A TEMPLATED ORMOSIL FILM ON AN ELECTRODE AND APPLICATION TO ELECTROCATALYSIS.

M. Ciabocco[1], M. Berrettoni[1], S. Zamponi[2], J. A. Cox[3]
[1]Dept of Chemistry, University of Bologna, Rimini Campus, via dei Mille 39, 47921-Rimini, Italy
[2]Dept of Chemistry, University of Camerino, via S. Agostino 1, 62032-Camerino, Italy
[3]Department of Chemistry and Biochemistry, Miami University, 701 E. High St., 45056-Oxford, OH 45056, USA

Modification of various electrodes with nanometer-scale organically modified silica (ormosil) films and with channels diameters controlled at 20-nm is described [1]. Electrochemically assisted deposition of sol-gel films yields microporous films on electrodes when the processing is at a sufficiently positive potential to generate hydrogen ion as the catalyst. In particular, with aminopropyltriethoxysilane, APTES, followed by immobilization of poly(styrene sulfonate), PSS, nanobeads (20-nm) used in conjunction with $(CH_3)_3SiOCH_3$ as the precursor, the resulting ormosil film contains approximately cylindrical channels with 20-nm diameters reflecting the PSS size. These channels are homogeneously distributed on the electrode surface. Cyclic voltammetry of $Ru(CN)_6^{4-}$ at this film-coated electrode with dispersed pores is consistent with the behavior of a nanoarray. The conductance is limited to the channels because the ormosil phase is non-conducting [2]. Applications with an electrochemically deposited catalyst, cobalt-hexacyanoferrate (CoHCF), in the channels were examined. The structure of this catalyst was nanoparticulate [3]. In this modified electrode, the amount of the electrochemically deposited CoHCF can be modulated within the channels, in order to obtain either CoHCF nanorods or CoHCF bulk. The latter forms when the amount of CoHCF overflows onto the ormosil surface. Electrocatalytic oxidation of cysteine was studied on CoHCF nanoparticles and successfully performed on these nanorod arrays. Greater catalytic activity than with bulk-form CoHCF was observed.

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VOLTAMMETRIC DETERMINATION OF IRON IN SEAWATER BY ATMOSPHERIC OXYGEN CATALYSIS IN 500 µL SAMPLES

S. Caprara[1], C. Dossi[2], D. Monticelli[1]
[1]Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, via valleggio, 11 – 22100 Como
[2]Dipartimento di Scienze teoriche e Applicate, Università degli Studi dell'Insubria, via Dunant, 3 – 21100 Varese

Iron plays a vital role in regulating primary productivity in vast areas of the ocean: low iron concentrations consistently found in high nutrient – low chlorophyll (HNLC) areas led to the formulation of the "iron hypothesis", the possibility that iron is the limiting agent for primary productivity in vast areas of the oceans. This limitation has important consequences on the regulation of the global climate via a reduction of the ability of the oceanic phytoplankton to sink atmospheric CO_2 and export a part of it to the deep ocean in a process referred to as the biological pump. Iron detection in seawater at the trace level was accordingly encouraged by fundamental research in oceanography. Dissolved iron analysis challenges the analytical chemist to reach extreme detection capabilities, prevent the high risk of sample contamination and tackle the issue of a high salinity matrix. Aim of this communication is to show the recent advancements developed in our research group by developing a new voltammetric method suitable for the determination of iron in seawater directly on board during scientific cruises. Adsorptive cathodic stripping voltammetry with catalytic enhancement was chosen as the analytical technique because it offers the possibility to reach this goal without employing a pre-concentration step. The ligand to be used for analysis was initially selected: 2,3-dihydroxynaphthalene (DHN) was chosen as it offers unrivaled sensitivity and the associated method is free from interferences. A first benefit of the devised method is the strong reduction of analysis time by eliminating the UV digestion usually needed for sample pretreatment. Moreover, the procedure features the use of atmospheric oxygen as a signal enhancer, thus further reducing the analysis time as the purge time for oxygen removal is not needed. Finally, the procedure introduced the use of a 500 µL sample holder, leading to a twenty-fold sample reduction with respect to existing methods. As a result, the setup method features a very low detection limit (5 pM iron) coupled to a very high sensitivity (around 50 nA/nm min^{-1}).

CHIRAL ELECTROANALYSIS ON ACHIRAL ELECTRODES IN "*INHERENTLY CHIRAL*" IONIC LIQUID MEDIA

P.R.Mussini,[1] S. Arnaboldi,[1] A. Gennaro[2], A.A. Isse[2], V. Michali,[1], S. Rizzo,[3] F. Sannicolò[1]
[1]Dip. di Chimica, Univ. degli Studi di Milano,Via Golgi 19 20133 Milano
[2]Dip. di Scienze Chimiche, Univ. degli Studi di Padova, via Marzolo 1, 35131 Padova
[3]CNR ISTM, via Golgi 19, 20133 Milano

To achieve chiral electroanalysis, an alternative strategy to using chiral electrodes is to work on achiral electrodes in a chiral medium. In this frame, chiral ionic liquids CILs should perform much better than chiral organic solvents, on account of their higher intrinsic order; and, by analogy with the recently introduced "*inherently chiral*" electrode surfaces of unprecedented enantiorecognition ability [1-3], "*inherently chiral*" ionic liquids ICILs should perform better than CILs.
To obtain ICILs we started from 3,3'-bicollidine, an inherently chiral atropo-isomeric bipyridine scaffold of easy synthesis, converting by dialkylation its antipodes into enantiopure bicollidinium double salts. With appropriate choice of the alkyl chain length and of the counter anion the melting points were lowered below room *T*, yielding enantiopure ICILs. Of these we highlighted the huge enantioselectivity in chiral voltammetry tests, employing them as low-concentration additives in commercial achiral ionic liquids like $BMIMBF_4$. The tests were performed on commercial achiral screen printed electrodes SPEs, using the same chiral probes previously used for testing inherently chiral surfaces. The enantiomer peak separation is huge, comparable to that obtained working with inherently chiral electrodes, and of course specular employing the (*R*) or (*S*) additive.
Importantly, similar and even better performances as low-concentration additives can also be obtained with smaller terms in the bicollidinium double salt series, solid at room *T* but of much easier synthesis. The enantiomer peak separation is modulated by the additive concentration (even reaching ~0.35V). The medium enantioselectivity holds with chemically different probes, even of applicative interest, like DOPA. Such results point to the possibility to obtain outstanding enantiodiscrimination on achiral electrodes even employing the new compounds as minority components in a commercial achiral medium.
(*With the contribution of Fondazione Cariplo, grant no. 2011-1851 "Inherently Chiral Ionic Liquids")*

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NEW MIMOSINE-BASED PEPTIDE AS CHELATING AGENT FOR MEDICAL USE.

J.I. Lachowicz[1], V.M. Nurchi[1], G. Crisponi[1], E. Randaccio[1], Z. Szewczuk[2], R. Bachor[2], P. Stefanowicz[2], X. Lopez[3], J.I. Mujika[3], G. Dalla Torre[3], M.A. Zoroddu[4], M. Peana[4], S. Medici[4]
[1]Dept. of Chemical and Geological Sciences, University of Cagliari, Cittadella Universitaria, 09042 Monserrato, Italy, lachowicz@unica.it
[2]Faculty of Chemistry, University of Wroclaw, F. Joliot Curie 14, 50-383 Wroclaw, Poland
[3]Kimika Fakultatea, Euskal Herriko Unibertsitatea PK 1072, 20080 Donostia, Spain
[4]Dept. of Chemistry and Pharmacy, University of Sassari, Via Vienna 2, I-07100 Sassari, Italy

Hydroxypyridinones are characterized by synthetic versatility and high affinity for a number of metal ions, making these ligands an excellent choice as therapeutic and/or diagnostic metallopharmaceuticals. The formation of exceptionally stable and, in many cases, neutrally charged complexes with a wide variety of metal ions, including the trivalent cations Fe^{3+}, Al^{3+}, Ga^{3+} and In^{3+}, as well as the actinides and lanthanides, is a common feature of hydroxypyridinones.[1]
Mimosine (ß-N(3-hydroxy-4-pyridone}α-amino propionic acid) is a toxic L-amino acid isolated from seeds of *Leucxena glauca* Berth (LBG) or *Mimosa pudica*.[2] Moreover, it is an extremely efficacious inhibitor of DNA replication in mammalian cells.[3, 4] The hydrolysis of mimosine leads to 3,4-hydroxypyridinone, similar to deferiprone, used since 2000 as iron chelator for β-thalassemia.
Here we will report a three-mimosine peptide with the best sequence for chelating Fe^{3+}, Ga^{3+} and Al^{3+} ions. Moreover, we will present the computational studies on the tailor-made peptides for octahedral coordination, the organic synthesis and the metal coordination studies.

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CHEMICAL MODELS FOR THE INTERPRETATION OF ACID/BASE CHEMISTRY AND COMPLEXATION CAPABILITY OF TANNIC ACID

S. Berto[1], M. Ginepro[1], V. Schettini[1], P. G Daniele[1]
[1]Dipartimento di Chimica, Università di Torino, Via P. Giuria, 7 – 10125 Torino

The tannic acid (TA) belongs to hydrolysable tannins class, natural polymers derived from vegetable kingdom and containing a carbohydrate molecule as central core esterified by hydroxybenzoic acids. Tannins show antioxidant and antibacterial properties. They can protect the cellular components from the oxidative damages and are able to reduce the growth of some kinds of fungi, bacteria and viruses[1]. Tannins are also dispersed in surface waters and have similarities with humic substances[2,3]. They can interact with both organic molecules[3] and metal cations. The presence of di-phenol groups leads to the formation of chelates with metals, but the complex formation tends to favour precipitation process[4].
Since the different and interesting aspects of these polymeric molecules, it could be interesting and useful to identify chemical models to explain properly their protogenic and complexation capabilities. In this work, chemical models for the TA were studied. pH-metric titrations were performed on aqueous solutions of TA. The titration curves present a wide buffered region in the pH range 6-9, as expected. This behaviour suggests the progressive dissociation of some of the phenolic groups. The data obtained were elaborated with the BSTAC[5] program and a chemical model that provides two main dissociation processes was proposed. The same systems were studied by spectrophotometry. This technique reveals the presence of a protonated and a deprotonated form of the TA. The spectra recorded were elaborated by HypSpec® software and it was possible to estimate an average protonation constant of the macromolecule. This value is in accordance with the chemical model proposed by the elaboration of pH-metric data. Discontinuous spectrophotometric titrations were conducted on the TA-Fe(II) systems and the stability constants of the TA-Fe(II) complexes were estimated.

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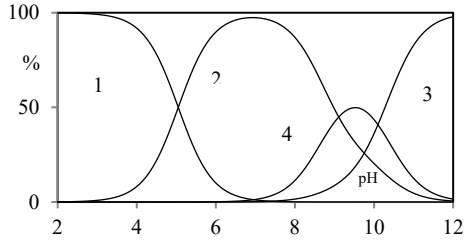
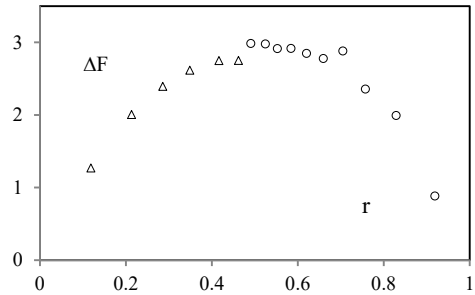
RHENIUM(I) TRICARBONYL COMPLEXES WITH AMINOACIDS IN AQUEOUS SOLUTION

G. De Tommaso[1], M. Iuliano[1], L. De Rosa[2], G. Malgieri[3], R. Fattorusso[3,5], A. Romanelli[4,5], L. D. D'Andrea[2,5], C. Isernia[3,5]
[1]Department of Chemical Sciences, University of Naples "Federico II" Via Cupa Nuova Cintia, 21– 80126 Naples (Italy).
[2]Institute of Biostructure and Bioimages CNR Via Mezzocannone, 16–80134 Naples (Italy).
[3]Department of Environmental Science and Technologies, Biological and Pharmaceutical, Second University of Naples, Via Vivaldi, 43–81100 Caserta (Italy).
[4]Department of Pharmacy, University of Naples "Federico II", Via Mezzocannone, 16–80134 Naples (Italy).
[5]Interuniversity Research Centre on Bioactive Peptides, Via Mezzocannone, 16–80134 Naples (Italy)

Organometallic tricarbonyl complexes of Rhenium(I) and Technetium(I), *fac*–$[M(H_2O)_3(CO)_3]^+$ (M = Re, Tc), especially the aqueous complexes, have recently assumed an important role for diagnostic and therapeutic applications. In this regard, *fac*–$[Re(H_2O)_3(CO)_3]^+$ cation is readily conjugated to biomolecules which contain coordinating N, P, O, S atoms [1], where one or more water molecules can be replaced by ligands to obtain very stable d^6 low–spin complexes [2]. Recently study has showed interaction between *fac*–$[Re(H_2O)_3(CO)_3]^+$ and histidine/imidazole molecule. Aim of this work is the study of the interaction among *fac*–$[Re(H_2O)_3(CO)_3]^+$ and some aminoacids that have been investigated using different instrumental techniques.





Potentiometric titrations conducted with glass electrode in the pH range 2–10 estabilish that a complexation effect is observed. Information on complexes formation can be obtained also by spectrophotometric UV–VIS and fluorimetric measurements in solutions with different metal/ligand ratio.

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3-HYDROXY-4-PIRIDINONE DERIVATIVES: SYNTHESIS, ACID - BASE PROPERTIES AND INTERACTIONS WITH Al^{3+}

K. Chand[1], R. M. Cigala[2], A. Irto[2], F. Crea[2], C. De Stefano[2], S. Sammartano[2], M. A. Santos[1]
[1]Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovísco Pais 1, 1049-001 Lisboa, Portugal
[2]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università degli Studi di Messina, Via Stagno d'Alcontres, 31 – 98166 Messina

The 3-hydroxy-4-piridinones (3,4-hydroxypiridinones) are a family of ligand derivatives of 1,2-dimethyl-3-hydroxy-4-pyridinone (commercially known as Deferriprone), which have been recently developed in view of applications in metal-chelation therapy and metal detoxication, because they are effective in all biological conditions and do not involve relevant undesired effects. [1,2] This contribution describes the synthetic procedures used in the preparation of a set of extrafunctionalized 3,4-hydroxypiridinones and the results of investigation of their acid-base properties and binding ability towards the metal cation Al^{3+} in aqueous solution.
They can be synthesized from the 3,4-hydroxypyranone (maltol) through a reaction of protection of the –OH group with a benzyl group, followed by a double Michael-type addition with opening and closure of the aromatoid ring. These compounds can be further derivatized via the formation of amide bonds and final deprotection of the hydroxyl group with a hydrogenation catalyzed by 10% Pd/C. [3]
The study of speciation of the 3,4-hydroxypiridinones in aqueous solution started from the investigation of their acid-base behavior, by performing spectrophotometric ($200 \leq \lambda/nm \leq 400$) and spectrofluorimetric measurements at I = 0.15 mol L^{-1} in $NaCl_{(aq)}$ and T = 298.15 K and at T = 310.15 K (physiological conditions). The analysis of experimental data allowed to refine the protonation constants of all these ligands, with values quite in accordance either between the two analytical techniques or with the literature data [4,5].
The binding ability of the 3,4-hydroxypiridinones towards the Al^{3+} was studied through potentiometric and spectrophotometric experiments carried out at T = 298.15 K and I = 0.15 mol L^{-1} in $NaCl_{(aq)}$. The speciation models are characterized by species ($Al_pL_qH_r$) with different stoichiometry. Finally, the sequestering ability of the ligands towards the chosen metal cation was investigated with the calculation of the $pL_{0.5}$, an empirical parameter already proposed by the research group [6], which represents the total concentration of ligand necessary to sequester the 50% of a given ion present in trace in solution.

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BRANCHED PEPTIDES AS NEW Cu(II) CHELATING AGENTS MIMICKING METALLOENZYME BINDING SITES

M. Remelli,[1] R. Guerrini,[1] N. Marchetti,[1] M. Perinelli,[2] M. Tegoni[2]
[1]Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Ferrara, Via Fossato di Mortara 17 – 44121 Ferrara
[2]Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze, 17/A – 43124 Parma

Branched peptides can be obtained from a central scaffold to which some peptide sequences are linked; they have been described in the preparation of novel promising antibacterial agents, vaccines and anticancer drugs [1].
In this contribution we describe the study of two Cu(II)-binding oligopeptides and of their tetrameric branched forms. The C-protected peptide sequences AAHAWG-Am (**P[1]**) and HAWG-Am (**P[2]**) were synthesized using solid phase synthesis. Their tetrameric branched derivatives were obtained by binding four identical chains of each peptide to a maleimide-functionalized cyclam platform, through a recently described procedure [2].
Monomeric peptide **P[1]** binds Cu(II) at its N-terminal site (Ala-Ala-His-). At physiological pH, spectroscopic data are fully consistent with a 1:1 Cu:peptide binding stoichiometry through a (N_{amine}, $2N_{amide}$, $N_{imidazole}$) donor atoms set, in agreement with literature [3]. Consistently, spectroscopic data for the tetrameric (**P[1]**)$_4$cyclam/copper(II) system showed that the tetrameric construct binds 4 equivalents of Cu(II) with the same coordination mode.
Monomeric peptide **P[2]** forms a bis-complex as the major species at pH 7. Spectroscopic data are consistent with a mixed Gly-like (N_{amine}, O) and histamine-like (N_{amine}, $N_{imidazole}$) coordination to the cupric ion, in the equatorial plane of the complex. On the other hand, at pH to 9, the coordination mode changes to a 1:1 species, where three deprotonated peptide nitrogen atoms are involved in the binding of Cu(II). Interestingly, the spectroscopic data on the corresponding tetrameric (**P[2]**)$_4$cyclam/copper(II) system suggest that at both pH 7 and 9 only two Cu(II) ions are bound to the macromolecule.
We aim now to use these scaffolds to prepare novel *de novo* designed copper peptides [4].

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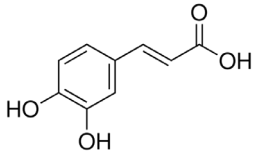
STABILITY CONSTANTS OF ALUMINIUM(III) COMPLEXES WITH CAFFEIC, FERULIC AND *p*-COUMARIC ACIDS IN AQUEOUS SOLUTION

E. Furia, A. Beneduci, R. Elliani, A. Tagarelli
Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci, 87036 Arcavacata di Rende

The aim of this work was to gain insight into the complexation properties of caffeic, ferulic and *p*-coumaric acids (**1**, **2** and **3** respectively) towards Al(III). The toxicity of metal has led several researchers to seek new strategies in the treatment of aluminium intoxication [1].



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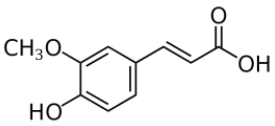

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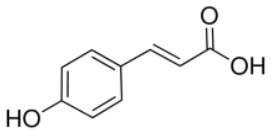

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Phenolic acids are a well-known family of natural compounds, present in fruit and plant components of our diet. Although the antioxidant *vs.* antiradical activity of caffeic, ferulic and *p*-coumaric acids has been studied in different model systems, few studies were performed towards gaining insight into their chelating properties towards aluminium cation. Therefore, knowledge of the stability of the phenolic acidmetal complexes is an important tool in the evaluation of their antioxidant mechanisms.
The protonation constants of the free ligands, H_2L, and the stability constants of the complexes were performed by potentiometry with a glass electrode in the physiological conditions (*i.e.* in 0.16 M NaCl and at 37°C), and the experimental data were analyzed by using a computer program [2].
The concentrations of ligands (C_L) and of Al(III) (C_M) were varied between ($0.5 \cdot 10^{-3}$ and $1.5 \cdot 10^{-3}$) mol·dm^{-3}, and the ligand-to-metal ratio was varied between 1 and 3 ($1 \leq C_L/C_M \leq 3$). The hydrogen ion concentration was varied from $1 \cdot 10^{-2.5}$ mol·dm^{-3} to incipient precipitation of basic salts which takes place in the range $[H^+] = 1 \cdot 10^{-4.5} - 1 \cdot 10^{-5.5}$ mol·dm^{-3} depending on the specific ligand to metal ratio. The general equilibrium can be written, schematically, for all the three systems as follow:

$$p\ Al^{3+} + r\ H_2L \rightleftarrows Al_pH_{-q}(H_2L)_r^{(3p-q)} + q\ H^+ \qquad \beta_{pqr}$$

The speciation model and equilibrium data were determined on the basis of potentiometric evidences as well as the bonding sites by means of ^{1}H- NMR spectroscopy.

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HYPCAL, A VERSATILE TOOL FOR THE DETERMINATION OF STANDARD REACTION ENTHALPY AND BINDING CONSTANT VALUES FROM CALORIMETRIC DATA

C. Sgarlata[1], C. Bonaccorso[1], M. Volkova[2], P. Gans[3], G. Arena[1]
[1]Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale Andrea Doria, 6 – 95125 Catania
[2]Ivanovo State University of Chemistry and Technology, Ivanovo, Russia
[3]University of Leeds, U.K. (retired)

HypCal is a new program developed for the simultaneous determination of both standard enthalpy of reaction and binding constant values in chemical systems of any complexity by making use of isothermal titration calorimetry data. The program does not impose limits on the chemical constitution of the system or on the quantity of experimental data to be analyzed. The chemical system is defined in terms of species of given stoichiometry rather than in terms of binding models (e.g independent, cooperative, etc.) [1,2]. Many titration curves may be treated simultaneously. HypCal can also be used as a simulation program when designing experiments. Typical applications are in studies of ligand protonation, host-guest reactions, metal-ligand complexation and competition reactions. HypCal may be used to process data from both partially filled and overfilled calorimeters.
The use of the program is here illustrated with sample data obtained with nicotinic acid [3]. Preliminary experiments were used to establish the different titration conditions for the two sets of titration curves that are needed to determine the thermodynamic parameters. The same advantageous experimental procedure has also been used to determine the species forming in solution and the relevant thermodynamic parameters for the binding of a sulfonato-calix[4]arene ligand with some pyridinium-based gemini guests in water at physiological pH [4]. Data obtained showed that guests having different size, shape and flexibility are able to form water-soluble homodimeric supramolecular capsules. The whole molecular recognition process is driven by different and often opposing forces including hydrophobic and electrostatic interactions.

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DETERMINATION OF OVER 60 DRUGS OF ABUSE IN HAIR BY PLE-DLLME EXTRACTION AND LC-HRMS ANALYSIS

C. Montesano[1], G. Vannutelli[1], F. Vincenti[1], A. Gregori[2], L. Ripani[2], D. Compagnone[3], M. Sergi[3], R. Curini[1]
[1]Department of Chemistry, Sapienza University of Rome, P.le A. Moro, 5 – 00185 Roma
[2]Department of Scientific Investigation (RIS-ROMA), Carabinieri, Viale Tor di Quinto, 119 – 00191 Roma
[3]Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Via Balzarini 1 – 64100 Teramo

Blood and urine are the conventional specimens to determine drug exposure; however, in the last twenty years hair testing has gained increasing attention. Hair is a unique material for the retrospective detection of drug consumption, due to its large detection window, and it is easy to collect, store and transport. The extraction of psychoactive substances from the inner of the hair structure is a critical point of the analytical process and different strategies have been proposed for this purpose. Hair incubation is often performed by digestion of hair matrix with NaOH. Alternative method consists in the incubation of hair with methanol or ethanol for several (4 to 18) hours [1]. Recently, our research group has proposed pressurized liquid extraction (PLE or ASE) demonstrating that this method offers excellent yields in a short time [2, 3].
In this work a multiclass method for the determination of both traditional drugs of abuse and new psychoactive substances (NPS) in hair has been developed. The analytes included all the most diffused drugs as well as new drugs belonging to the classes of synthetic cannabinoids, cathinones and phenetylamines. The main metabolites are also included in the method in order to differentiate between passive exposure and effective assumption. The extraction of drugs is based on PLE extraction while the clean-up is carried on by dispersive-liquid liquid microextraction (dLLME). This miniaturized technique uses a very low amount of extraction solvent resulting in considerable enrichment factors for the tested compounds
The detection was performed by liquid chromatography coupled with high resolution mass spectrometry (LC-HRMS). The use of HRMS as detection technique allows to easily add new analytes in the method with minimal validation steps.

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TRACE DETECTION OF IMPROVISED EXPLOSIVES DEVICES (IED) FROM HUMAN HANDS: A PROMISING FORENSIC TOOL

R. Risoluti[1], A. Gregori[2], L. Ripani[2], S. Materazzi[1]
[1] Department of Chemistry – "Sapienza" University of Rome p.le A.Moro 5, 00185 Rome Italy
[2] Carabinieri RIS – Scientific Investigation Department – v.le Tor di Quinto, 151, 00191 Rome Italy

The screening of persons for the explosive traces detection has become more important in the last decades due to an increased threat of terroristic attacks, as some type of explosives can be prepared from easily obtainable ingredients [1]. Especially at the airport, check points or other security relevant public or military areas, a robust and efficient screening technology is desired which offers a high level of security and guarantees a high throughput.
The most prevalent form of explosive device utilized by terrorists today is the Improvised Explosive Device (IED). IEDs are homemade, non-conventional explosives, fabricated by combining common chemicals [2]. A large number of explosives such as RDX (hexogen), TATP (triacetone triperoxide), TNT (trinitrotoluene), pyrotechnic charge, dynamite, smokeless gunpowders, blackpowder, among others, can be considered for the preparation of IEDs, thus the sensitivity, and stability may be unpredictable.
In this work, a fast real-time easy-to-use method for the detection of IED manipulation based on Near Infrared Spectroscopy (NIRs) coupled to chemometrics has been developed for the identification of explosives from human hands. Moreover, the persistence of traces evidences was elaluated over time, considering time between handling and analysis as well as the daily routines related to hand washing.
The parallel obtained results from official reference method (GC-MS) in cooperation with italian Scientific Investigation Department (Carainieri-RIS of Rome) demonstrated the proposed approach to be promising for the real time detection of explosive species in forensic investigations.
In addiction, the proposed method has the advantage of simplicity, avoiding sample pretreatment procedures, non-invasive and non-destructive measurements, which is considered as the optimal technological characteristics involving the analysis of an explosive or other forensic materials. The achieved results, highlight the extremely high potential of NIRs combined with chemometrics for the fast and easy identification of explosive residues and additionally, its potential ability to detect the explosive manipulation.
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BROAD SCREENING AND IDENTIFICATION OF NOVEL PSYCHOACTIVE SUBSTANCES IN PLASMA BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY – HIGH RESOLUTION MASS SPECTROMETRY AND POST-RUN LIBRARY MATCHING

C. Montesano[1], G. Vannutelli[1], A. Gregori[2], L. Ripani[2], D. Compagnone[3], M. Sergi[3], R. Curini[1]
[1]Department of Chemistry, Sapienza University of Rome, Piazzale A. Moro, 5 – 00185 Roma
[2]Department of Scientific Investigation (RIS-ROMA), Carabinieri, Viale Tor di Quinto, 119 – 00191 Roma
[3]Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Via Balzarini 1 – 64100 Teramo

Drug abuse is today a growing global problem. Often the consumers are not aware about the type of substances they are using and the correlated risks. In recent years, new psychoactive substances (NPS) appeared in the illicit market. These substances are new molecules, natural or synthetic, which are sold in smart shops as incense, bath salts or standard not for human use. The presence of NPS, such as synthetic cathinones, cannabinoids and phenethylamines, which are known to be pharmacologically and toxicologically hazardous, has been frequently reported. More than 500 new psychoactive substances (NPS) have been notified in EU since 2005. The report 2016 of the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA), reveals that the number of new substances has not declined in the past year with 100 new substances reported for the first time in 2015 [1].
The aim of this study was the development of a liquid chromatography–high-resolution mass spectrometry (LC-HRMS) method for a broad screening of NPS in plasma. Data acquisition was in MS/MS and full-scan modes and the method was validated for 25 NPS belonging to different chemical classes (Training Set). Quantitative results have been obtained for these analytes with limits of quantification ranging from 0.03 to 0.4 ng/mL.
The method was proven to be suitable for a wide screening of additional substances, included an in-house database containing over 300 NPS and known metabolites. To this aim, a post-run library matching was conducted for every sample with the library, which may be constantly expanded with new drugs, in order to obtain an effective screening of NPS in biological matrices.

[1] EMCDDA 2016. Avaible at: http://www.emcdda.europa.eu/publications/eu-drug-markets/2016/in-depth-analysis

EFFICIENT HYDROGEN PRODUCTION BY g-C_3N_4: CORRELATION BETWEEN PHYSICO-CHEMICAL PARAMETERS AND VISIBLE-LIGHT PHOTOCATALYSIS

A. Speltini[1], F. Maraschi[1], M. Sturini[1], A. Profumo[1], C. Milanese[1], L. Sangaletti[2], G. Drera[2], M. Patrini[3], G. Guizzetti[3], L. Malavasi[1,4]
[1]Dipartimento di Chimica, Università di Pavia, via Taramelli 12, 27100 Pavia, Italy
[2]I-LAMP, Dipartimento di Matematica e Fisica, Università Cattolica del Sacro Cuore, Brescia, Italy
[3]CNISM, Università di Pavia, via Bassi 6, 27100 Pavia, Italy
[4]Dipartimento di Chimica, Università di Pavia, e INSTM, via Taramelli 12, 27100 Pavia, Italy

Graphitic carbon nitride (g-C_3N_4), the newest carbon-based 2D material made of layered sheets of tri-s-triazine connected via tertiary amines, is now attracting great interest in photocatalysis. In particular, application of g-C_3N_4 for hydrogen gas (H_2) photoproduction from water has tremendous potentiality due to the large visible-light absorption and low recombination rate of electron-hole pairs [1]. Here, we present a systematic investigation of the physico-chemical properties of g-C_3N_4 samples prepared from different precursors (dicyandiamide, melamine, urea) and at different condensation temperatures (500-700°C), and their H_2 photoproduction efficiencies. The latter were studied under simulated solar light (500 W/m^2, for 6 h), on 21 mL triethanolamine aqueous solutions (10% v/v), in presence of 1 g/L catalyst (3 wt% Pt). Results clearly evidenced a correlation between both precursor type and condensation temperature with the photocatalytic efficiency, and the key parameter affecting the efficiency resulted to be the surface area of the final g-C_3N_4 material. The best results were obtained using urea as precursor with polymerization at 650°C, leading to a H_2 production yields up to ca. 4350 μmoles/g/h. The batch-to-batch reproducibility was verified on independent samples (RSD ca. 11%).

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ENERGY RETURNED ON ENERGY INVESTED (EROEI) IN ANALYTICAL CHEMISTRY

M. Innocenti[1,3], A. Giaccherini[1], F. Di Benedetto[2], A. Lavacchi[3], H.A. Miller[3], N. Cioffi[4], R.A. Picca[4] and F. Vizza[3].
[1]Dipartimento di Chimica, Università degli Studi di Firenze, Via della Lastruccia, 3 – 50019 Firenze.
[2]Dipartimento di Scienze della Terra, Università di Firenze, via G. La Pira4, 50121,Firenze.
[3]Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR and INSTM Consortium, 50019 Sesto F.no, (Florence).
[4]Dipartimento di Chimica, Università degli Studi di Bari, via Orabona 4, 70126, Bari.

In the last few years a sector of Analytical Chemistry relating to the research of analyses and increasingly accessible analytical methodologies, of low cost, fast and adaptable to customers often inexperienced in chemistry has spread. The world energy situation (despite this period of low cost oil due to reasons far removed from the market itself) with a growth in demand and a forced reduction of the energy supply has given more importance to the factor EROEI (Energy Returned On Energy Invested). This coefficient, which when referred to a given energy source indicates its convenience in terms of energy output, has arrived in many research areas becoming an important parameter to evaluate, compare and make strategic choices, in our case, of analysis of the different analytic techniques that can be used to determine and characterize an analyte. With this type of approach will be presented works in different fields of analytical research but with the same quest for energy sustainability. In the field of catalysis we will present not only the search for new catalysts for fuel cells but also the study of complete processes having acceptable EROEI [1]. With the same objective will be presented recent results in the field of solar cells with low environmental impact [2,3]. Finally, in the same perspective, new spectroscopic analytical methods in the food sector that are not only based on precision and accuracy but also on all the parameters discussed above will be presented [4].

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REGIOCHEMICAL ASSIGNMENT OF SULFOQUINOVOSYL-DIACYLGLYCEROLS IN PARSLEY AND SPINACH LEAVES EXTRACTS BY REVERSED-PHASE LC-ESI-MS/MS

S. Granafei[1], P. Azzone[1], I. Losito[1,2], C.D. Calvano[1,2], F. Palmisano[1,2], T.R.I. Cataldi[1,2]

[1] Dipartimento di Chimica, [2] Centro Interdipartimentale SMART, Università degli Studi di Bari Aldo Moro, Via E. Orabona, 4 - 70126 Bari

Sulfoquinovosyldiacylglycerols (SQDG) are sulfolipids occurring in photosynthetic tissue of many eukaryotic and prokaryotic species, characterized by a sulfoquinovose moiety as polar head group. The regiochemical characterization of SQDG based on the fragmentation pattern observed in tandem MS spectra is still an open issue due to the conflicting rules concerning the interpretation of mass spectral features [1–3]. Collision induced dissociation (CID) of the $[M-H]^-$ precursor ion generates, along with the carboxylate ($R_{1/2}COO^-$) and sulphite (SO_3^-) ions, diagnostic product fragments coming from the neutral losses of the acyl chains linked to sn_1/sn_2 positions of the glycerol backbone, as fatty acids ($[M-H-R_{1/2}COOH]^-$) or as ketenes ($[M-H-R_{1/2}=C=O]^-$). Some Authors suggested the use of the relative intensity of carboxylate anions cleaved from sn_1 and sn_2 for regiochemical assignment [4]. However, it is well known that extra fragmentation of these ions may occur (especially by increasing the unsaturation degree) making the above rule of doubtful general applicability. An alternative rule is based on the relative intensity of the $[M-H-R_{1/2}COOH]^-$ ions [2]. To definitely prove the general validity of such viewpoint for regiochemistry assessment of SQDG, lipid extracts of parsley and spinach leaves were analysed by LC-ESI-(CID)MS/MS, as such and after an enzymatic treatment by phospholipase A1 (PLA1), specifically catalyzing the cleavage at the sn_1 position, forming *lyso*-sulfolipids. The parsley sample, which is known to contain the predominant SQDG 34:3 (*m/z* 815.5), gave the corresponding *lyso* form SQMG 0:0/16:0 after PLA1 treatment, thus confirming that the product ion resulting from sn_1 FA loss is the preferred one.

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CHROMATOGRAPHIC AND MASS-SPECTROMETRIC METHODS OPTIMIZATION FOR THE UNTARGETED ANALYSIS OF COMPLEX PHYTOCHEMICAL MIXTURES

C. Cavaliere, G. La Barbera, R. Samperi, A.Laganà.
Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", P.le Aldo Moro, 5 00185-Roma

Untargeted profiling is a major challenge in metabolomics because of the wide abundance of different compounds in a complex matrix. Due to their rapid development, high resolution mass spectrometry (HR-MS) instrumentations are now able to provide the accurate masses of unknown compounds, extending the coverage of metabolites in untargeted profiling. However, when treating with complex phytochemical mixtures, HR-MS is usually interfaced with a separation technique such as ultra high performance liquid chromatography (UHPLC) [1]. As a matter of fact, the separation step is fundamental because it provides retention times as additional identity information and allows to distinguish several isomeric compounds. The quality of the chromatographic peaks has an important effect on the output of the data processing, making crucial the optimization of chromatographic and mass spectrometric conditions for the identification step.
In this work, a systematical evaluation of different chromatographic systems and mass spectrometric methods is presented. Strawberry extracts were used for assessment of each chromatographic and mass-spectrometric condition. An UHPLC coupled to a Q-Exactive mass spectrometer was employed. Accurate mass ion chromatograms obtained for each chromatographic and mass-spectrometric method were processed by the open source software MZmine v2.19 [2]. Briefly, a list of ions for each scan was generated. A chromatogram was built for each mass that could be detected continuously over the scans, and then deconvoluted into individual peaks. The LC–MS detected features were filtered removing isotopes and the interferences from the solvent blank. The different chromatographic and mass spectrometric methods were evaluated based on the number of detected and fragmented features, on the number of data point for each peak, on the peak shape quality. Based on the results obtained, the best chromatographic and mass-spectrometric method was used to tentatively identify about 100 compounds by means of the search on a home-made database, confirming the importance of a good chromatographic and mass-spectrometric optimization in order to extend the coverage of a complex matrix metabolic profile.

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UHPLC COUPLED TO HIGH RESOLUTION MASS SPECTROMETRY FOR THE EVALUATION OF NON-INTENTIONALLY ADDED SUBSTANCES (NIAS) FROM FOOD CONTACT MATERIAL

A. Cavazza, C. Bignardi, C. Laganà, P. Salvadeo, C. Corradini
Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze, 17/A – 43124 Parma

UHPLC coupled to high resolution mass spectrometry (HR-MS) is a very useful and effective technique for the identification of unknown compounds released by food contact materials [1]. The present study was aimed at the identification and the monitoring of several compounds by UHPLC coupled to Orbitrap technology through a both targeted and untargeted approach. In particular, the investigation was focused on the identification of non-intentionally added substances (NIAS), sometimes found in a product without a clear explanation about their origin. They may represent impurities of raw materials, or may derive from degradation of their components.
An important point regards re-usable plastic containers and kitchen equipment for food storage and processing. They are generally used for several years, and are subjected to ageing and mechanical damage due to repeated use and frequent washing cycles. Chemical and physical ageing provoke tiny scratches and small cracks formation on the surface, that become potential source of oligomers generated by material decomposition [2].
This research was focused on the analysis of simulants and food put in contact with re-usable objects of different age, made of polycarbonate for food contact. The untargeted analysis allowed the identification of polymer products of degradation and colouring agents.
Results showed a different pattern of oligomers deriving from materials of different age, allowing to discriminate between new and old samples. Traces of colouring agents were also found to be released, and were recorded in higher amount from new samples than from old ones.
The identification of these molecules shows the high potential of the technique and its importance in the field of food control. It represent a relevant issue that deserves great attention in terms of safety concern, together with the estimation of a potential threshold effect for risk assessment.

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STUDY OF THE TRANSFORMATION PRODUCTS OF THEV SWEETENER STEVIOSIDE BY USING HIGH RESOLUTION MASS SPECTROMETRY

M. Sarro[1], C. Medana[2], V.A. Sakkas[3], P. Calza[1]
[1] Department of Chemistry and NIS Centre of Excellence, University of Torino, via P. Giuria 7, 10125 Torino, Italy
[2] Department of Molecular Biotechnology and Health Sciences, University of Torino, via P. Giuria 5, 10125 Torino, Italy [3]
[3] Department of Chemistry, University of Ioannina, Ioannina 45110, Greece

Stevioside is a glycoside extracted from the *Stevia Rebaudiana* plant, which is widely used as sweetener in foods. Sweeteners are nowadays considered as emerging contaminants; due to their high stability under biological, physical and chemical treatment, they were found in natural waters at concentration up to micrograms per liter levels. LC/MS is the most widespread technique employed for the analysis of sweeteners thanks to its high sensibility, specificity and accuracy.
In our work, we investigated the stevioside photostability and its photoinduced transformation over time; in particular, we focused on the identification of its transformation products and the assessment of their toxicity. Analyses were performed *via* LC-HRMS employing a LTQ-Orbitrap mass spectrometer and an ESI ion source both in positive and negative mode. Mass spectrometry allows the identification of unknown compounds and their structural characterization by the fragmentation of the obtained ions. Along with the stevioside decomposition, we identified more than one hundred unknown transformation products, most of them in the form of several isobaric species. By employing accurate mass determination, we were able to attribute an empirical formula to each species and through MS^n analyses we were capable to characterize the detected transformation products and to distinguish several isobaric species. The overall transformation mechanism was assessed and involved the hydroxylation/oxidation of the molecule and the subsequent loss of the glucoses bound to the parent compound. Acute toxicity of stevioside and its derivatives was evaluated as well using the *Vibrio Fischeri* bacteria.

P. Arbeláez, F.Borrull, E. Pocurull, R. Maria Marcé, J. Chromatogr. A 1393 (2015) 106-114

LIQUID EI (LEI) INTERFACE: A NEW CONCEPT FOR INTERFACING LIQUID CHROMATOGRAPHY AND ELECTRON IONIZATION MASS SPECTROMETRY.

V. Termopoli, G. Famiglini, P. Palma, M. Piergiovanni, A. Cappiello.
LAB LC-MS, Dipartimento di Scienze Pure ed Applicate, Università di Urbino, Italy

Direct-EI LC-MS interface is a technique that combines, in a single instrument, the identification advantages of library searchable, electron ionization (EI) spectra with the separation power of an UHPLC column, without the drawbacks of matrix effects and the cost of a high-resolution instrument. Unknown identification is of increasing importance in food safety, environmental, forensic and many other applications where the complexity of the matrix is a troubling factor. The advantage of EI for tentative identification of GC amenable compounds is unparalleled. Expansion of EI fragmentation to a wider variety of molecules in a liquid phase provides an attractive alternative to identification and offers a complementary technique to high-resolution/high mass accuracy LC-MS instrumentation and atmospheric pressure techniques. However, due to the active metal surface as well as the small ion source volume, adsorption and thermal degradation phenomena occur, resulting in peak tailing and reduce chromatographic response, especially for those compounds with low-volatility and high-molecular weight. To solve these problems and to generally adapt the Direct-EI interface to a wider range of ion sources and instrument types we came up with a radical but simple interface design. The new interface design is called “Liquid-EI”, LEI to distinguish it from the original device. In a LEI interface, vaporization of the UHPLC eluate is carried out inside a suitable, independent micro-channel right before entering the ion source. This channel is at the moment obtained inside a GC-MS transfer line that becomes an active part of the system. An inert gas flow carries the gas phase molecules into the ion source. This solution moves the solute vaporization event immediately outside the ion source into a more suitable space in terms of dimensions, temperatures and surface materials, and free of sensitive components and electric potentials. The LEI interface was mounted on an Agilent 7010 QQQ mass spectrometer and coupled with an Agilent 1290 Infinity UHPLC system (Agilent Technologies, Santa Clara, CA, USA). The flow rate was split at approximately 500 nL/min before entering the interface. Preliminary results, carried out using the 7010 system, gave us an optimistic impression. Preliminary experiments were conducted using chlorotalonil and its metabolits, giving good results in terms of robustness, sensitivity and repeatability. Further studies will be oriented to fully unveil the potential of the interface and to test it in very different applications.

LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY METHOD FOR THE DETERMINATION OF VITAMIN K HOMOLOGUES IN BREAST MILK

A. Gentili[a], A. Micchelli[a], P. Tomai[a], M.E. Baldassarre[b], R. Curini[a], V. Pérez-Fernández[a]

[a] Department of Chemistry, Faculty of Mathematical, Physical and Natural Science, "Sapienza" University of Rome, Piazzale Aldo Moro 5, P.O. Box 34, Posta 62, 00185 Rome, Italy.

[b] Department of Biomedical Sciences and Human Oncology, University of Bari Aldo Moro, Piazza Giulio Cesare 11, 70124 Bari, Italy.

Human milk is the only source of vitamin K for exclusively breastfed neonates. This vitamin is crucial both for the blood coagulation (vit K_1) and for the normal neurological and skeletal development of foetus and newborn (vit K_2). Since vitamin K is ubiquitous in foods, its deficiency is not usual in adults, but plasma levels and hepatic storage are really low at birth due to the limited placental transfer and hepatic storage capacity of the foetus. Maternal consumption of vitamin K antagonists and/or inadequate nutrition during pregnancy are other factors which may contribute to a serious neonatal hypovitaminosis K [1], which can lead to a hematologic disorder of the newborn known as " vitamin K deficiency bleeding" [1, 2], negative repercussions on bone mineralization and neurological development of the infant [2].

In light of the functions provided by this "precious" micronutrient, it is clear the importance of verifying the adequate supply to the exclusively breastfed infants. For this reason, the determination of the several vitamin K homologues in human milk is a topic of great interest that has not still been completely elucidated. This paper presents a HPLC-MS/MS method for the simultaneous determination of phylloquinone, menaquinone-4 (MK-4), and menaquinone-7 (MK-7) in human milk after an effective and simple isolation procedure. Overnight cold saponification and extraction of the analytes with hexane has provided yields above 75% and limits of detection (LODs) below 0.8 ng/mL. After a complete validation study, the method was applied to measure vitamin K congeners in several human milk samples, finding vitamin K_1 concentrations comparable with those reported in the literature. In addition, this is the first study performed for the determination of MK-4 and MK-7 in Italian women maternal milk.

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METAL-NANOPARTICLE DECORATED SILICON NANOWIRES FOR LDI-MS APPLICATIONS

R.A. Picca[1], M.J. Lo Faro[2], C.D. Calvano[1], B. Fazio[2], S. Trusso[2], P.M. Ossi[3], F. Neri[4], C. D'Andrea[5], A. Irrera[2], N. Cioffi[1]
[1]Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via E. Orabona, 4 – 70126 Bari
[2]IPCF-CNR, viale F. Stagno d'Alcontres 37, Faro Superiore, 98158 Messina
[3]Dipartimento di Energia & Center for NanoEngineered Materials and Surfaces-NEMAS, Politecnico di Milano, Via Ponzio, 34-3, 20133 Milan, Italy
[4]Dipartimento di Fisica e di Scienze della Terra, Università di Messina, V.le F. Stagno d'Alcontres 31, 98166 Messina, Italy
[5]MATIS IMM CNR e Dipartimento di Fisica, Università degli Studi di Catania, Via Santa Sofia 64, 95123 Catania

Nanomaterial-based platforms are continuously proposed for laser desorption/ionization mass spectrometry (LDI-MS) applications, especially when the detection of low molecular weight (LMW) analytes (below 700 *m/z*) is pursued [1]. Advantages of nanostructured surfaces reside on the use of lower laser fluences, higher signal intensity, and reduced number of interferences in comparison to conventional matrixes. Either metal nanoparticles (e.g. Ag-, AuNPs) [2], and semiconductor nanowires (e.g. SiNWs) [3] have been successfully applied as LDI-MS tools. However, the combination of both nanomaterials has not yet been fully explored in this field. Here, we present highly dense arrays of SiNWs, prepared by a maskless wet-etching technique, assisted by the deposition of an ultrathin gold film on a Si substrate [4], for the LDI-MS analysis of different LMW molecules. Moreover, their decoration with metal NPs, using an additional pulsed laser deposition stage [5], allows preparing functionalized platforms. In the latter case, LDI-MS experiments carried out using AgNP-decorated SiNWs showed how metal nanophases were more effective than bare SiNWs, especially for the detection of molecules bearing unsaturated bonds. Material characterization data were also correlated to MS results.

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PRESS-PRINTED CONDUCTIVE CARBON BLACK NANOPARTICLES FILMS FOR MOLECULAR DETECTION AT THE MICROSCALE

F. Della Pelle[1,2], L. Vázquez[3], M. Del Carlo[2], M. Sergi[2], D. Compagnone[2], A. Escarpa[1]
[1]Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, Faculty of Biology, Environmental Sciences and Chemistry, University of Alcalá E-28871 Alcalá de Henares, Madrid, Spain
[2]Faculty of Bioscience and Technology for Food, Agriculture and Environment University of Teramo 64023, Teramo, Italy
[3]Institute of Materials Science of Madrid (CSIC) C/Sor Juana Inés de la Cruz Nº 3, Cantoblanco, 28049 Madrid, Spain

Carbon black nanoparticles (CBNPs) press-transferred films-based transducers for molecular detection at the microscale were proposed for the first time. Current sensing atomic force microscopy (CS-AFM) revealed that CBNPs films were effectively press-transferred, retaining their good conductivity. A significant correlation between the morphology and the resistance was observed. The highest resistance was localized at the top of the press-transferred-film protrusions whereas low values are usually obtained at the deep crevices or grooves. The amount of press-transferred CBNPs is the key parameter to obtain films with improved conductivity; which is in good agreement with the electrochemical response. In addition, the conductivity of such optimum films was not only ohmic; in fact, tunneling/hopping contributions were observed, as assessed by CS-AFM. The CBNPs film was employed as detector coupled to microfluidic chip confirming the remarkable properties, offering low detection potentials and negligible surface fouling. CBNPs films acted as exclusive electrochemical transducers as evidenced by using two classes of molecules, neurotransmitters and environmental organic contaminants. These results revealed the potential of these CBNPs press-transferred films for opening new avenues in microfluidics and other related micro and nano chemistry applications.

NEW APPLICATIONS OF ENZYMATIC (OR NOT ENZYMATIC) DMFC DEVICES USED AS ANALYTICAL TOOLS: ANALYSIS OF PHARMACEUTICAL TINCTURES OR ACTIVE PRINCIPIA (WITH ALCOHOLIC GROUP) AND BIOLOGICAL FLUIDS.

M. Tomassetti, R. Angeloni, G. Merola, S. Marchiandi, M. Castrucci, L. Campanella.
Dipartimento di Chimica, Università di Roma "La Sapienza", p.le Aldo Moro, 5, 00185 Roma.

Recently our research group has continued the analytical research, devoted to the use of Direct Methanol Fuel Cell (DMFC) employed for analytical purposes [1]. The research reported in this communication concerns several new analytical applications, one of which regarding the opportunity to determine two particular antibiotics having an alcohol functional group in their molecule, that is Imipenem and Chloramphenicol. The second new application was the possibility of improving the features, from the analytical point of view, of the catalytic fuel cell for methanol and ethanol, by introducing an enzyme, immobilized into a dialysis membrane small bag, in the anodic area of the fuel cell. This aim has been achieved, particularly using the enzyme alcohol dehydrogenase, which increased the sensitivity of the method and reduced dramatically the response time of the cell. Using this enzymatic DMFC device the ethanol content of several pharmaceutical tinctures have also been checked. In this case obtained results have been compared both with the ethanol content declared by the producer firms and with data obtained analyzing the same samples using an amperometric catalase enzyme sensor, recently pointed out in our laboratory. In conclusion in this research, it has been firstly demonstrated as the fuel cell can be useful to determine, in real matrices, also other organic molecules, which contain an alcoholic function (although with a much lower sensitivity than methanol or ethanol). Finaly, using an enzymatic DMFC device, it can be reach the goal concerning a drastic reduction of the measurement time of the fuel cell used for analytical purposes, enhancing at the same time also its sensitivity. Lastly, owing the low cost, the very low encumbrance of the cell and the measurement apparatus [1], the high sensitivity and short response time achieved by the enzyme alcohol dehydrogenase addition in the fuel cell, this small enzymatic DMFC can be also improved as a device able to check the ethanol concentration in the test for the measurement of the alcoholic level in "breath test" of drivers, performing simulated analysis of serum, or saliva; all these goals have been reached.

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A MODULAR MECHANISM TO REGULATE THE AFFINITY OF NUCLEID-ACID TARGET-RESPONSIVE NANOSWITCHES

E. Del Grosso[1], A. Idili[1], A. Porchetta[1], G. Palleschi[1], F. Ricci[1].
[1]Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma "Tor Vergata", Via della Ricerca Scientifica, 1 - 00133, Roma.

Here we demonstrate a general and modular approach to regulate the activity of target-responsive DNA-based nanoswitches.
In recent years several target-responsive DNA nanodevices have been rationally designed to recognize a wide variety of molecular inputs and, in response to the binding, perform a specific function. For example, DNA-based nanoswitches have been largely employed as sensing nanodevices to detect specific DNA sequences, proteins, antibodies and other relevant targets. In order to improve the performances of the above described target-responsive DNA-based nanodevices, novel strategies would be needed to control their activity in a more flexible way.
Motivated by the above arguments, here we demonstrate a highly modular strategy to introduce an external control in the functionality of nucleic acid target-responsive nanoswitches. We did so by coupling together two DNA-based responsive elements: a triplex-forming recognition element, that binds a sequence-specific DNA target through a clamp-like mechanism involving both Watson-Crick and Hoogsteen interactions and a second functional responsive unit which can be, for example, a split aptamer selected to bind a small molecule. In the presence of the specific target of one of the above responsive elements, the nanoswitch partially folds and its ability to bind the second target is restored. Our strategy is highly modular and flexible, for this reason, the roles of the two recognition elements used can be easily exchanged and we can finely modulate the affinity of both, DNA-recognition elements and aptamers, using an external ligand. The modular nature of our strategy makes it easily generalizable to different DNA based recognition elements. As a demonstration of this we successfully designed five different DNA nanoswitches whose responsiveness can be regulated by different molecular effectors and targets.
The convenience with which this mechanism is designed suggests that it may prove a useful tool by which sensors, genetic networks and other biotechnology devices employing nucleic-acid based receptors can be controlled with an external input.

AMPEROMETRIC GENOSENSOR ENHANCED BY DENDRIMER-LINKED PNA PROBES: COMPETITIVE VS NONCOMPETITIVE APPROACH

M. Giannetto, S. Fortunati, A. Rozzi, M. Mattarozzi, A. Manicardi, R. Corradini, M. Careri
Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze 17/A 43124 Parma

Genosensors base their recognition element on the interaction between nucleobases in nucleic acids, either natural, synthetic or mimics. In a research program dealing with the development of innovative sensors as powerful analytical tools for assessing food safety[1,2] we combined performance of DNA-mimic probes based on Peptide Nucleic Acids (PNA) with the enhancing properties of Polyamidoaminic (PAMAM) dendrimers. The findings of our previous studies[3], focused on the use of the same PNA probes on all-gold Screen Printed Electrodes (SPEs), evidenced as best results those obtained suiting a non-competitive approach, based on the binding of target DNA by a PNA-Capture Probe (CP)-functionalized sensor, followed by the hybridation with a properly synthesized Ferrocene-tagged PNA-Reporter Probe (RP). In this prototype, the CPs were immobilized on the electrodic surface via Self Assembled Monolayers (SAM) from mercaptoundecanoic acid. Although this methodological approach allowed us to detect the DNA target (transgenic soy 15-mer sequence) at nanomolar scale, the non-competitive approach required the use of low concentrations of immobilized CP, thus reducing sensitivity of the genosensor. With the double aim of amplifying response of the device and simultaneously optimizing the conformational freedom of the bound CP strands (15-mer PNA) we combined the use of Glassy Carbon-Gold Nanoparticles GC-GNP SPEs functionalized by covalent immobilization of a 1.5 generation PAMAM dendrimer, featuring an ethylenediamine core and 16 carboxyl-addressed terminal groups (Figure 1). Preliminary experiments showed highly promising results, with an amplification effect by two orders of magnitude in terms of current recorded upon the same concentration of the CP used to functionalize the electrodic surface. This strategy will be investigated by developing both competitive and non-competitive DNA-assay protocols aimed at specific recognition of transgenic material at trace levels, as possible contaminants of GMO-free foods.

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MIP NANOPARTICLES AS ASCORBIC ACID SCAVENGER IN ELECTROCHEMICAL MEASUREMENTS

R. Rapini[1], F.Canfarotta[2], G. Marrazza[1], S. Piletsky[2]
[1]Department of Chemistry "Ugo Schiff", University of Firenze, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy
[2]Chemistry department, Leicester University, Leicester LE1 7RH, UK

Detection of small molecules is still one of the most important targets for analytical methods based on biosensors, because of the fact that biomolecules or bio-mimetic molecules used as probe interact more easily with bigger targets, such as proteins or nucleic acid chains. Over the last few years, the use of biosensors (like immunosensors or enzyme-based sensors) has been reported as a promising alternative to traditional methods for the analysis of small molecules with biological relevance thanks to the possibility to combine lower costs coupled with efficient analytical performances. Antibodies, e.g., have been used for years in biological assays, biosensor development and diagnostic tests, because of their capacity to selectively bind themselves to a specific target molecule, even within a complex sample. Nevertheless, antibodies have some disadvantages: they are expensive to produce, they usually exhibit low stability, batch-to-batch variability and poor performance in non-physiological conditions (e.g. in organic solvents). Compared to classical bio-molecular probes, the use of artificial receptors has changed the point of view in biosensors development: the possibility to easily synthesise the probe molecule give a great advantage respect to the classical enzyme-based sensors and immunosensors and the use of synthetic probes makes easier the realisation of sensible and stable detectors for small molecules. In this way, the use of molecular imprinted polymers (MIPs) combined with innovative approaches based on disposable screen printed electrochemical cells as transducers, gave us the possibility to develop a new way for small molecules analysis. We developed the synthesis of MIP nanoparticles able to sequester ascorbic acid from tested solution in order to suppress its signal in electrochemical measurements in which the target can interfere. MIP nanoparticles have been characterised using DLS (dynamic light scattering) and UV-absorption ad their activity has been studied in aqueous solutions.

IMPROVED DIRECT ELECTRON TRANSFER COMMUNICATION BETWEEN CELLOBIOSE DEHYDROGENASE AND A GOLD ELECTRODE MODIFIED WITH A RIGID SELF-ASSEMBLED MONOLAYER AND GREEN METAL NANOPARTICLES: THE ROLE OF AN ORDERED NANOSTRUCTURATION

P. Bollella[1], L. Gorton[2], G. Favero[1], F. Mazzei[1], R. Antiochia[1]
[1]Department of Chemistry and Drug Technologies, Sapienza University of Rome, P.le Aldo Moro 5, 00185 – Rome, Italy
[2]Department of Analytical Chemistry/Biochemistry,P.O. Box 124, 221 00 – Lund, Sweden

Studies of direct electron transfer (DET) between redox enzymes and electrodes represent an area of extensive research for developing bioelectronic devices such as biosensors and biofuel cells [1]. However, most enzymes are not able to give DET because of the position of the active site of the enzyme, which is usually deeply buried within the protein structure [1]. Nanomaterial-modified electrodes are able to promote efficient DET reactions. Among all nanomaterials, metal nanoparticles (MNPs) play an important role in electrode modification because of their large surface area-to-volume ratios for protein loading as well as their excellent biocompatibility [2].
The aim of this work was to improve the DET efficiency between cellobiose dehydrogenase from *Corynascus thermophilus* (*Ct*CDH) [3,4] and a novel gold electrode platform, obtained by covalent linking of green AuNPs and AgNPs with a dithiol self-assembled monolayer, biphenyl-4,4'-dithiol (BPDT). The green AuNPs and AgNPs were synthesized using quercetin as reducing agent at room temperature. The *Ct*CDH/AuNPs/BPDT/AuE and *Ct*CDH/AgNPs/BPDT/AuE electrode platforms were compared with naked AuE, BPDT/AuE and MNPs/AuE in absence and in presence of lactose, in order to investigate the effects of different electrode modifications on DET.
The modified electrodes were successively used to develop an eco-friendly biosensor for lactose detection. The *Ct*CDH/AuNPs/BPDT/AuE based biosensor showed the best analytical performances and was successfully tested to quantify lactose content in real milk and cream samples.

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NANOSTRUCTURED SCREEN PRINTED ELECTRODES AND FOURTH GENERATION IONIC LIQUIDS AS USEFULL TOOLS FOR THE DEVELOPMENT OF PORTABLE BIOSENSORS

D. Zappi, R. Caminiti, S. Gabriele, C. Sadun, E. Scarpellini and M.L. Antonelli
Dipartimento di Chimica, Università degli Studi La Sapienza, p.le A. Moro, 5 – 00185 – Roma – Italy – daniele.zappi@outlook.it

Various types of modified electrodes have been prepared and tested to assembly and construct portable sensing devices, useful to analyze in a simple, fast and economic way substances of analytical interest in agrifood.
The Glassy Carbon electrode (GCE) surface has been modified with three nanomaterials: Multi-Walled Carbon Nanotubes (MWCNT), Graphene (GPH) and Gold Nanoparticles (GNP) [1]. To further optimize the electrochemical properties of the nano-modified electrodes, three RTILs of fourth generation were immobilized on the working electrode. The RTILs used in this study were all Choline based with the following aminoacids: Glycine (GLY), Serine (SER), and Phenylalanine (PHE) [2].
The electrochemical properties of each combination of nanomaterial and ionic liquid by cyclic voltammetry were studied. Bare GC electrodes of the Screen Printed type (SPE), with silver as reference electrode (SSE), have been used for modification. By immobilizing the proper enzyme onto the modified electrode surface, specific amperometric biosensors can be designed useful to determine different compounds of analytical interest [3].
Analytes such as antioxidant components in the extra-virgin oils, phenols in wines, alcohol in beverages and glucose in food matrices have been tested, using the proper enzyme respectively: microbial lipase from *Candida cylindracea*, laccase from *Trametes versicolor* (Tvl), alcohol dehydrogenase (ADH) and glucose oxidase (GOD).
The presence of nanostructured materials on the electrode active surface and their interaction with the ionic liquids, brings to an increased surface area for the interaction between analyte and receptor, consequently to an amplification of the amperometric signal and then to a higher sensitivity. Moreover, the new ionic liquids of fourth generation, prepared and characterized by our research group, are absolutely nontoxic, water soluble and enable the electron transfer between enzymes and electrode, by facilitating and strengthening the redox reaction observed.

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CONDUCTIVE POLYMER NANOCOMPOSITE BASED IMPEDIMETRIC IMMUNOSENSOR FOR 2,4-DICHLOROPHENOXY ACETIC ACID DETECTION

G. Fusco[1,2], C. Tortolini[1], A. D'Annibale[2], A. De Mico[2,3], R. Antiochia[1], G. Favero[1], F. Mazzei[1]
[1]Department of Chemistry and Drug Technologies, Sapienza University of Rome, Italy
[2]Department of Chemistry, Sapienza University of Rome, Italy
[3]Institute of Molecular Biology and Pathology - National Research Council, Italy

One of the best promising application field of the biosensors technology is the screening of pollutants in real sample matrices, due to the selectivity towards the analyte and the rapid, reproducible and possibly quantitative or semi-quantitative response.
2,4-Dichlorophenoxy acetic acid (2,4-D) is an auxinic herbicide with grown regulator activity that has been widely used for controlling broadleaf weeds in cereal grain crops. Because of its carcinogenic, teratogenic and estrogenic activity, the presence of residues of 2,4-D in agricultural products and environment can be extremely harmful for both humans and animals.
In this work, we developed an impedimetric label free immunosensor for the detection of 2,4-D herbicide either in standard solution and spiked real samples. For this purpose, we prepared by electropolymerisation a conductive poly-(aniline-co-3-aminobenzoic acid) (PANABA) based nanocomposite and then we immobilized anti-2,4-D antibody employing the carboxylic moieties as anchor sites. The nanocomposite was synthesized by electrochemical polymerization of aniline and 3-aminobenzoic acid, in the presence of a dispersion of gold nanoparticles, onto a multi walled carbon nanotubes based screen printed electrode. Aniline-based copolymer, together with the nanomaterials, allowed to enhance the electrode conductivity thus obtaining a wider dynamic impedimetric response and a more sensitive antigen detection. The impedimetric measurements were carried out by electrochemical impedance spectroscopy (EIS) in faradic condition by using $Fe(CN)_6^{3-/4-}$ as redox probe.
The developed impedimetric immunosensor displayed a wide linearity range toward 2,4-D (1-100 ppb), good repeatability (RSD 6%), stability and a LOD (0.3 ppb) lower than herbicide emission limits.

THE ROLE OF PAPER IN ELECTROCHEMICAL (BIO)SENSING BREAKTHROUGH

S. Cinti, F. Arduini, G. Palleschi, D. Moscone
Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma "Tor Vergata", Via della Ricerca Scientifica, 1 – 00133 Roma

Beyond the development of sensitive and accurate analytical devices, nowadays the attention is being focused particularly toward the lowering of three fundamental aspects: fabrication cost, user-tasks, and waste management. Among different technologies and materials, paper is representing a key-role over the construction of smart platforms both in optical and electrochemical fields. Paper demonstrated a high synergy when coupled with facile fabrication technologies such as wax- and screen-printing. Depending on several requirements such as the analytical needs, the sensing strategy, the field of operation, and the sample matrix, different typologies of paper represent valuable substrates capable of providing a "lab-in-a-hand". Herein, we report the application of paper-based electrochemical platforms in all the relevant analytical fields, i.e. environmental, clinical, and food areas. By using all-in-one approach, organophosphorus pesticides were detected in river and waste waters at ppb levels. By exploiting the filtering and storing capabilities of filter paper, all the (bio)reagents necessary to carry out the electroanalytical assay were stored in a designed test area just around the screen-printed electrode nanomodified with Carbon Black/Prussian Blue nanoparticles. Instead, office-paper was successfully used for the assembling of two different devices for practical uses in food and clinical samples. An alcohol oxidase-based biosensor was developed for the evaluation of ethanol in commercial beers. After the optimization of the analytical parameters such as pH, enzyme concentration and working potential, the biosensor allowed a facile quantification of ethanol up to 10 mM with a sensitivity of 16.2 μA/mM cm^2 and a detection limit equal to 0.52 mM. These satisfactory performances made this paper-based biosensor a useful device for the analysis of ethanol in four different types of beers, including Pilsner, Weiss, Lager and alcohol-free.
The detection of zinc ions in serum and sweat was performed using a paper based bismuth-modified screen-printed electrode. Under the optimised conditions of bismuth concentration, accumulation time, frequency, step potential, the zinc ions were detected at ppm levels, in agreement with the concentrations usually found in serum and sweat samples.

DETECTION OF DIMETHOATE IN WHEAT USING A MIP-GLASSY CARBON ELECTRODE COUPLED TO MICROEXTRACTION BY PACKED SORBENT (MEPS)

D. Capoferri, M. Del Carlo, M. Sergi, F. Di Ottavio, D. Compagnone
Facoltà di Bioscienze e Tecnologie Agroalimentari e Ambientali, Università degli Studi di Teramo, Via C. Lerici, 1 – 64023 Mosciano S.A. (TE)

Dimethoate is an organophosphate pesticide that induces toxicity through inhibition of acetylcholinesterase (AChE), leading to accumulation of acetylcholine. The aim of this work was the development of a simple, sensitive and selective method for analysis of dimethoate residues in wheat. The method consists of a microextraction by packed sorbent (MEPS) that allows the analyte extraction and pre-concentration, followed by MIP-glassy carbon electrode (MIP-GCE) detection. Microextraction by packed sorbent (MEPS) is a new format for solid-phase extraction (SPE) that has been miniaturized to work with small sample volumes. Moreover it is fast, simple and requires minimal volumes of solvents [1]. In the MEPS the sample preparation takes place on the packed bed containing 1-2 mg of sorbent. The extraction is performed by drawing sample through the syringe manually or by an auto-sampler. When the sample is passed through the solid support, the analytes are adsorbed to the extracting media. Finally the analytes are eluted with an organic solvent [2]. Molecularly imprinting is a process by which selected functional monomers are polymerized around a target analyte (template). After polymerization, the template molecule is extracted and a polymer matrix, which is complementary in shape and functionality to the template, is obtained. Thus, the polymer has the ability to selectively link to the target analyte [3]. In this work the dimethoate-polypyrrole MIP films were electropolymerized by cyclic voltammetry on the surface of glassy carbon electrode (GCE), with pyrrole serving as the monomer and dimethoate as the template. Dimethoate is electro-inactive, therefore an electroactive $K_3[Fe(CN)_6]$ solution was used as the probe in the electrochemical measurements for the indirect quantification of dimethoate observing the diminishment of the either oxidation or reduction peaks.

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FLEXIBLE, BIOCOMPATIBLE AND DISPOSABLE PH AND TEMPERATURE SENSORS BASED ON CARBON NANO-STRUCTURED MATERIALS

B. Melai[1], N. Calisi[1], P. Salvo[1], C. Paoletti[1], E. Herrera[1], V. Mollica[1], R. Fuoco[1] and F. Di Francesco[1]
[1]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via G. Moruzzi, 13 – 56124 Pisa

About 1.5 - 2 % of people experiences a chronic wound in the course of life, but this figures are deemed to increase in Western countries due to the ageing of population. Wearable sensors are creating great expectations for improving knowledge on the biochemical processes in action in these wounds and combining quality of treatment and low cost. SWAN-iCare is a project funded by the European Commission developing temperature, pH and metalloproteases activity sensors for monitoring and managing chronic wounds, mainly diabetic foot ulcers and venous leg ulcers. In this specific application, strict requirements in terms of flexibility, biocompatibility and low cost have been defined due to the use in direct contact with the wound bed.
We report here the fabrication, testing and validation of a resistive sensor based on reduced graphene oxide for the measurement of temperature and a potentiometric sensor based on graphene oxide for the measurement of pH in the wound bed. In-vitro validation with model solutions and real samples established an accuracy of 0.5 °C in the range 20-40 °C and 0.2 pH units in the range 5.5-9.0. Issues concerning biocompatibility for the use in contact with the wound bed are also addressed.

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SELF-STANDING COATINGS BASED ON POLY(2-HYDROXYETHYL-METHACRYLATE) FOR AMPEROMETRIC SENSING

C. Zanardi[1], S. Riso[1], M. Degli Esposti[2], P. Fabbri[2], R. Seeber[1]
[1] Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via G. Campi 103, 41125 Modena, Italia, chiara.zanardi@unimore.it
[2] Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna, via Terracini 28, 40131 – Bologna

As a novel approach to amperometric sensing, we discuss the performance of disposable electrode coatings based on a poly(2-hydroxyethyl-methacrylate) film stably bearing different redox mediators. The material can form self-standing films that can be mass-produced on an inert support and transferred onto the electrode surface before use. Thanks to the characteristics of the polymer matrix to swell by incorporation of large amounts of water, redox active species covalently bound to the polymer are in intimate contact with the electrolytic solution and, hence, with the potentially electroactive species inside.
As a proof of concept of the potentialities of this innovative approach, ferrocene was tested as a first redox active group to be included in the polymer coating. The capability of such a redox couple to act as the redox mediator with respect to proper substrates in solution, namely hydroquinone and ascorbic acid, was tested both in a static solution and in a flux cell. Quite interestingly, the sensor system exhibits very fast responses, resulting well effective also in flow injection analyses, over a wide concentration range.
As a further step in the application of these novel electrode coatings, enzymes can be linked to the polymer coatings, leading to biocatalytic electrode systems. As a first enzyme to test the effectiveness of this approach, glucose oxidase was linked to the polymer membrane by exploiting carboxyl moieties present in the film. Different chemical formulations of the membranes, as well as different methods to anchor the enzyme to the polymer membrane have been tested in order to achieve high sensitivity and fast response time in the analysis of glucose in standard solutions.
The performance of the sensor has been firstly evaluated by considering both cyclic voltammograms and chronoamperometric responses registered in static solutions of glucose at different concentrations. As a further step, the possibility to use the sensor in a flux cell has been attempted also in this case. Finally, the sensor has been tested for the determination of glucose in real matrices.

CHARACTERIZATION OF NANOMATERIALS USING A DYNAMIC SURFACE TENSION DETECTOR (DSTD) AND DYNAMIC LIGHT SCATTERING

M. Marongiu, V. Della Porta, B. Campanella, E. Bramanti
Istituto di Chimica dei Composti Organo Metallici, ICCOM-CNR Pisa

Currently, few data are reported on the toxicity due to the exposure to nanomaterials. A complete risk and safety assessment requires their comprehensive physical-chemical characterization, including chemical composition, size, morphology, surface area, crystallinity, and other physical-chemical properties.
The DSTD is a drop-based analyzer that provides real-time dynamic surface pressure measurements of components injected in an aqueous mobile phase. The DSTD is a pressure sensor-based instrument, which measures the changing pressure across the liquid/air interface of 2-4 microliter drops repeatedly forming at the end of a capillary. It has been widely applied in conjunction with Flow Injection Analysis (FIA) and High Performance Liquid Chromatography (HPLC) to the study of surface activity of polymers and proteins [1, 2].
In this work the FIA-DSTD apparatus has been applied to the measure of the dynamic surface tension of nanofluids, containing silver (Ag-NPs) and titanium dioxide nanoparticles (TiO_2-NPs) suspended in bidistilled water. These nanoparticles have been analysed in the framework of the characterization of nanomaterials form the NANoREG project [3], which is the first FP7 project aimed to get information on Environmental Health and Safety (EHS) issues of nanomaterials by the scientific evaluation of available data and new test methods. DLS measurements were also performed as support to DSTD data.
The DSDT data showed that Ag-NPs are surface active.
DSTD flow injection analysis of TiO_2-NPs showed that NM100 (anatase polymorph phase, 110 nm diameter, no organic coating) and NM101 (anatase polymorph phase, 6 nm diameter, organic coating) did not give any signal. NM103 (rutile polymorph phase, 25 nm diameter, organic coating) solutions showed, instead, intense DSTD signal. The calibration curve of NM103 was linear from 0.3 to 3.5 mg/mL and reached a *plateau* approximately above 50 mg/mL. The high surface activity of TiO_2-NPs NM103 may be due to its hydrophobic rutile polymorph phase, in agreement with the literature data. Both DSTD and DLS confirmed that NM103 particles tend to agglomerate and the agglomeration depends on their concentration.
The understanding of the surface tension properties of nanofluids may support the study of their complex interaction with biological macromolecules and, thus, provide useful insights into cytotoxicity, inflammatory potential and other key properties of these novel materials.

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A LOW COST CARBON BLACK MODIFIED SENSOR TO DETECT FREE CHLORINE IN WATER SAMPLES

M. Tomei[1], D. Neagu[2], F. Arduini[1], D. Moscone[1]
[1]Dipartimento di Scienze e Tecnologie Chimiche, Università degli studi di Roma "Tor Vergata", Via della Ricerca Scientifica, 1 – 00133 Roma
[2]Tecnosens S.r.l, Via della Ricerca Scientifica, snc – 00133 Roma

Chlorine is the most used chemical agent for the disinfection of swimming pools and drinking water, due to its high oxidizing power. The most known disinfectant is sodium hypochlorite, but other chlorine derivatives are also used. In aqueous solution there is an equilibrium between hypochlorite ion and hypochlorous acid, and the sum of these two species is defined as "free chlorine". The official method for the chlorine detection is the N, N-diethyl-p-phenylenediamine spectrophotometric method (DPD); its commercial variants allow to detect free chlorine *in-situ*, but they are less sensitive.
The target of this work was the development of a sensitive and low cost electrochemical sensor for the *in-situ* determination of free chlorine in water. The sensor was made using screen-printed electrodes modified with carbon black (CB), material chosen for its electrocatalytic properties.[1-2] The first step was the optimization of working conditions (amount of CB, potential value, pH and ionic strength of working solution) to obtain the best sensitivity and repeatability of the probe.
In particular, the working graphite electrode has been modified through drop casting with 10 µl of CB dispersion 1 mg/ml in N,N-Dimethylformamide /H_2O 1:1 (v/v). The amperometric study, conducted by applying a potential of -0.1 V vs. Ag/AgCl, has shown that the sensor possesses a linearity range between 0.05 and 200 ppm (R^2= 0.995), a sensitivity of 0.32 ± 0.02 µA/ppm, and a LOD of 0.01 ppm, calculated as three times the S/N. After studying the matrix effect of the swimming pool water and drinking water, the accuracy of the sensor was estimated. The percentage recoveries were respectively (97 ± 10) % in the swimming pool water and (70 ± 14) % in tap water, were satisfactory and confirmed the possibility to use the developed sensor in real samples.

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DETECTION OF ANTI-TISSUE TRANSGLUTAMINASE BY NANOELECTRODE ENSEMBLE BIOSENSORS FOR CELIAC DISEASE DIAGNOSTICS

P. Ugo, H.H. Baye, S. Longo
Università Ca' Foscari Venezia. Department of Molecular Sciences and Nanosystems. Via Torino 155 Mestre, Venezia (Italy).

Celiac disease (CD) is a gluten-induced autoimmune disorder with prevalence of about 1%, with increasing trend. In order to reduce the morbidity and the mortality associated to CD, it is important to develop simple and effective methods that allow to perform screening tests in the general population for an early diagnosis of the disease as well as follow-up tests able to manage the regression of the disease while the patient is on a gluten-free diet.
It has been demonstrated that the blood levels of anti-tissue transglutaminase (anti-tTG) correlate with the degree of the intestinal mucosal damage and that levels of this antibody increase when the celiac patient assume gluten; consequently, many recent research efforts are aimed at developing tests to detect anti-tTG in serum samples.
Anti-tTG immunoglobulins are classified into two isotypes, namely IgA and IgG. Immunoglobulin A (IgA anti-tTG) is the isotype typically determined as target analyte for serological CD screening. However, IgA-deficient CD patients are not identified by this analysis. Moreover, focusing on CD diagnosis in very young children for whom biopsy is not an eligible test, it has been found that only 87% of CD patients younger than 2 years of age showed high serum levels of IgA anti-tTG. On the other hand, serological diagnosis based on IgG assays, at present, does not look as a valid alternative for general screening because IgG based ELISA assays show poorer clinical sensitivity and specificity than IgA based analysis.
With the aim of overcoming the above described limits, here we present a novel electrochemical immunosensors based on nanoelectrode ensembles (NEEs) able to detect, with suitable sensitivity and selectivity, both the IgG and IgA isotypes of anti-tTG.
To this aim, we exploit the characteristics of NEEs prepared by template electroless deposition of gold in track-etched polycarbonate membranes with pores of 30 nm diameter. To obtain the sensor, the PC of the NEEs, is functionalized with tissue transglutaminase (tTG) as the capture antigen. The obtained immunosensors bind both the isotypes IgA and IgG of anti-tTG from serum samples. The selective detection of the two isotypes is possible by recognition using two differently labelled secondary antibodies: anti-IgG sec-Ab labelled with horseradish peroxidase (HRP) and anti-IgA sec-Ab labelled with glucose oxidase (GOx), respectively. In the first case, in the presence of IgG anti-tTG as the target analyte, the addition of HRP substrate (hydrogen peroxide) and hydroquinone as redox mediator generates an electrocatalytic

increase of the cathodic current related to the reduction of benzoquinone to hydroquinone. For the detection of the IgA isotype, glucose (substrate) and (ferrocenyl-methyl)trimethylammonium (redox mediator), are used to develop an anodic electrocatalytic signal, related to the oxidation of the ferrocenyl derivative to the ferricinium species. In both cases, relevant signals scale with the concentration of the relevant immunoglobulin isotype. The analytical performances of the NEE-based immune sensor are evaluated by determining both IgA and IgG anti-tTG in human serum samples and comparing the sensor's data with fluoro-enzyme immune assay results. Prospects for application to molecular diagnostics are discussed.

EXPLOITING MULTICOLOR LUCIFERASES FOR SMARTPHONE-BASED BIOLUMINESCENCE CELL BIOSENSORS

L. Cevenini[1], M.M. Calabretta[1], A. Lopreside[1], G. Tarantino[1], E Michelini[1,2], A. Roda[1,2].
[1]Department of Chemistry "G. Ciamician", University of Bologna Via Selmi, 2, Bologna, Italy
[2]INBB, Istituto Nazionale di Biostrutture e Biosistemi, Viale Medaglie d'Oro 305, Roma, Italy

The aim of this work is to exploit bioluminescent (BL) proteins (luciferases) emitting at different wavelenghts for the development of cell biosensors using the smartphone-camera as detector.
Several luciferase genes were isolated from luminescent organisms and luciferase variants with improved emission properties (e.g. red-shifted emission wavelengths, higher quantum yield emission, stable kinetics) were also obtained by mutagenesis of corresponding genes. These enzymes have been widely used for the development of bacterial, yeast and mammalian cell biosensors to perform pharmaceutical, environmental and food analysis. The use of living cells for biosensing provide useful infomation about the bioavailability of target analyte and, exploiting the intracellular signalling pathways it is possible to obtain information about the actual biological activity of a sample. The increasing interest of using smartphones to develop integrated analytical devices is mainly due to the wide diffusion of such devices which are equipped with powerful processor, sensitive BSI-CMOS camera and offer several built-in functionalities such as connectivity, data elaboration, geo-tagging and the possibility to develop custom application. We previously demonstrated the feasibility of implementing enzyme-based and cell-based assays with bio-chemiluminescence detection into smartphone [1,2].
Here, yeast (S.cerevisiae) and mammalian (Hek293T, HepG2) cells were genetically engineered to respond to different compounds/stimuli (e.g. inflammatory and antioxidant stress, xenobiotics, heat shock, heavy metals, hormones) with the expression of different BL reporters, in order to select the optimal combination of luciferases providing robust cell biosensors with adequate analytical performances in terms of LOD, dynamic range and response time, for smartphone-based biosensing.

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APPLICATION OF AN ELIME ASSAY FOR THE DETECTION OF SALMONELLA IN VEGETABLES

L. Fabiani[1], G. Volpe[1], E. Delibato[2], E. Pucci[2], S. Piermarini[1], G. Palleschi[1]
[1]Department of Chemical Science and Technologies, University of Tor Vergata, Via della Ricerca scientifica 1 Roma.
[2] Department of Veterinary Public Health and Food Safety, Istituto Superiore di Sanità, viale Regina Elena 299, Rome.

Traditionally foodborne illnesses were mainly caused by food of animal origin, but more recently they are associated to the consumption of fruit and vegetables, in which *Salmonella* represents the main source of contamination. The European legislation has established that this pathogen must be absent in a defined amount of a given food product (25g for vegetable) [1]. The standard cultural method for *Salmonella* (ISO 6579) is very sensitive, inexpensive, but requires up to 5 days to obtain results. Therefore, a rapid, sensitive and specific method to detect this pathogen is needed.
In our previous work, a rapid, low-cost and easy-to-use ELIME (Enzyme-Linked-Immuno-Magnetic-Electrochemical) assay, has been developed and successfully applied to irrigation water, the primary source of vegetable contamination [2]. The system employs magnetic beads (MBs) as support of a sandwich immunological chain, coupled with a strip of 8-SPEs.
In this work we present the application of the ELIME assay in vegetables to detect the presence/absence of *Salmonella enterica*, focusing the attention on *S.* Napoli and *S.* Thompson (serotypes responsible for various community alerts due to the consumption of vegetables). In particular, the system was applied to blank vegetables (resulted negative for salmonella by ISO method), experimentally inoculated with 1-10 CFU of S. Napoli or S. Thompson for 25 g of sample, pre-enriched in two different broths: BPW and BPWc. In both cases aliquots were taken at different incubation times in order to establish the best medium and the minimum pre-enrichment time necessary to reveal salmonella. The same experiments were performed in parallel using RTi-PCR assay and a confirmation with the ISO culture method was carried out. Comparing the effectiveness of the two media, the use of BPWc provides a better discrimination of both *Salmonella* serotypes from the control. Using the selected BPWc medium, 20 and 8 h of pre-enrichment incubation were sufficient to reveal the presence of *Salmonella* with ELIME assay and RTi PCR, respectively. It is important to stress that the pre-enriched phase is typically requested to allow the growth of viable cells, overcoming the problem of the inability of PCR and ELISA based methods to distinguish between living and dead cells. Although the RTi-PCR was found to be more rapid than ELIME assay, the advantage of the ELIME is the employment of a cost effective and portable instrument that can be used in decentralized

laboratories by not highly qualified staff, for a widespread control of salmonella in vegetables.

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A DNA NANODEVICE THAT LOADS AND RELEASES A CARGO WITH HEMOGLOBIN-LIKE COOPERATIVITY

D. Mariottini[1], A. Idili[1], A. Vallée-Bélisle[3], K. W. Plaxco[2], F. Ricci[1].
[1] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata,Via della ricerca Scientifica 1, 00133 Roma
[2] Department of Chemistry and Biochemistry, University of California, Santa Barbara
[3] Département de Chimie, Universite´ de Montréal, Laboratory of Biosensors and Nanomachines, Québec QC H3T 1J4, Canada

In nature, the control of molecular responsiveness is often achieved using "Hill-type" cooperativity, a mechanism in which sequential binding events on a multivalent receptor are coupled such that the first enhances the affinity of the next, producing a steep, higher-order dependence on target concentration. Here, we rationally designed a synthetic DNA nanodevice that mimics such cooperativity mechanism and respond to its specific target with a Hill-type curve. To do so, we designed a clamp-like DNA nanoswitch that contains multiple interacting binding sites. These binding sites recognize the same target DNA through a triplex-forming clamp-like mechanism. The first binding event affects the affinity of the subsequent binding events thus resulting in a steeper dose-response curve with Hill coefficients experimentally indistinguishable from the theoretically expected maximums. We have been able to modulate the cooperativity by changing the experimental conditions such as pH and temperature obtaining results comparable to natural macromolecules such as hemoglobin.

TIMING IN ANALYTICAL PYROLYSIS: Py(HMDS)-GC/MS OF GLUCOSE AND CELLULOSE USING ON-LINE MICRO REACTION SAMPLER

M. Mattonai, D. Tamburini, E. Ribechini, M.P. Colombini,
Dipartimento di Chimica e Chimica Industriale, Università di Pisa
Via Moruzzi 13, 56124 Pisa, Italy

The study of carbohydrates by analytical pyrolysis is a thriving field, not only for its numerous applications, but also for its constant search of innovation and self-improvement. *In situ* derivatization has recently become a powerful technique for improving the resolution of the pyrograms and the detectability of the pyrolysis products [1]. The main drawback of this method is the generation of partially derivatised compounds, which generate complex chromatograms and lower the reproducibility of the results.
In this work, a novel method based on Py-GC/MS with *in situ* silylation is presented for the first time. A micro reaction sampler [2] was used to simultaneously obtain the pyrolyis reaction and facilitate the derivatisation of pyrolysis products of glucose and cellulose, by enabling the materials to react with the derivatising agent (hexamethyldisilazane, HMDS) in a sealed glass capsule at high temperatures and for long periods of time. This drastically improved the silylation of the pyrolysis products and the chromatographic resolution, and reduced the complexity of the pyrograms obtained with respect to a conventional fast pyrolysis experiment. In particular, the partial silylation of anhydrosugars, among the main pyrolysis products, was almost completely overcome after ten minutes of reactive pyrolysis.
Different results were also obtained for glucose and cellulose in terms of predominant pyrolytic pathways. The formation of anhydrosugars, in particular levoglucosan, was the preferential pyrolytic reaction for glucose. The formation of cyclopentenones and small fragmented molecules with up to three carbon atoms was predominant for the pyrolysis of cellulose.
This work discloses a powerful and potentially widely applicable analytical method for the investigations of organic materials under controlled pyrolytic conditions with the advantage of increasing the effectiveness of *in situ* derivatisation.

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COMBINATION OF CAPILLARY ELECTROPHORESIS, QUALITY BY DESIGN, NMR AND MOLECULAR MODELING FOR IMPURITY PROFILING: DEFINITION OF THE DESIGN SPACE AND INVESTIGATION OF INTERMOLECULAR AFFINITIES, COMPLEXATION AND SEPARATION MECHANISMS

S. Furlanetto[1], S. Orlandini[1], B. Pasquini[1], F. Melani[3], C. Caprini[1], M. Innocenti[2], M. Del Bubba[2]
Dipartimento di Chimica "U. Schiff", Università degli Studi di Firenze, [1]Via U. Schiff 6 – [2]Via Della Lastruccia 3 – 50019 Sesto Fiorentino, Firenze
[3]Dipartimento di NEUROFARBA, Università degli Studi di Firenze, Via U. Schiff 6 – 50019 Sesto Fiorentino, Firenze

Quality by Design principles have been applied for the set-up of various capillary electrophoresis (CE) methods for the determination of drugs, of their related substances and their enantiomeric purity. The use of a risk-based approach in the development of a separation method for impurity assay has been recently reported with success, as it makes it possible an in-depth understanding of parameters affecting analytical method performances. The design space (DS) concept requires the definition of a multidimensional region where the quality of analytical data is assured with a selected probability and can be defined by means of mathematical models representing a step forward in the comprehension of the electrophoretic behaviour of the analytes. Pseudostationary phases involving micelles, microemulsions and cyclodextrins (CDs) were used for CE separation. Molecular Dynamics (MD) and NMR studies were employed to elucidate separation mechanisms, host-guest interactions and intermolecular affinities and confirmed the CE experimental results. Aspects such as the affinity pattern of analytes towards various CDs as well as the equilibrium constants and the structure of complexes were addressed. The effect of cosurfactant *n*-butanol and the role of ionic surfactant sodium dodecyl sulphate (SDS) on separation selectivity were investigated. Capacity factors and effective mobilities of the solutes were calculated and compared with the potential and the gain energy of inclusion complexes of analytes with surfactant and cosurfactant. MD simulations and NMR experiments underlined the ability of CDs of including the SDS monomer forming inclusion complexes and the pivotal role of this surfactant in modulating the different affinities of the analytes for chiral selectors.

MASS TRANSFER IN NEW CHIRAL STATIONARY PHASES DEVELOPED ON CORE-SHELL AND SUB-2μm FULLY POROUS PARTICLES FOR ULTRAFAST CHIRAL SEPARATIONS

A. Cavazzini[1], M. Catani[1], L. Pasti[1], F. Gasparrini[2], O. Ismail[2]
[1] Department of Chemistry and Pharmaceutical Sciences (University of Ferrara) Via L. Borsari 46 - 44121 Ferrara (Italy)
[2] Dipartimento di Chimica e Tecnologie del Farmaco (University of Rome, La Sapienza) P.le A. Moro 5 - 00185 Roma (Italy)

The great advancement in the development of highly efficient packing materials for liquid chromatography has only partly touched chiral separations. This has been due both to practical problems in the synthesis and functionalization with chiral selectors of sub-2-μm particles and to the lack of the understanding of mass-transfer mechanisms in chiral chromatography. In this presentation, we focus on new chiral stationary phases (CSPs) for enantioselective ultra-high-performance liquid chromatography (e-UHPLC) prepared by using silica particles of different characteristics (fully porous and core shell particles) and dimensions, including sub-2 μm totally porous silica particles, as base materials. Columns of different geometries were prepared by high-pressure slurry packing and employed to perform a deep evaluation of the kinetic performance of the new stationary phases by means of an approach combining stop-flow (peak parking) and high-flow rate measurements.
The potential of these new CSPs, in particular Whelk-O1 brush-type ones, for ultrafast chiral separations is investigated by using very short columns (down up to 10 mm length) and in terms of method transfer from e-HPLC to e-UHPLC. Remarkably, on a 10×3.0 mm column, the normal-phase separation of trans-stilbene oxide was achieved in less than 1 sec (flow rate: 8ml/min), with a chromatographic resolution larger than two.

HIGH EFFICIENCY MULTIDIMENSIONAL GAS CHROMATOGRAPHY COUPLED TO ISOTOPE RATIO MASS SPECTROMETRY AND QUADRUPOLE MASS SPECTROMETRY SIMULTANEOUS DETECTION

D. Sciarrone[1], A. Schepis[1], L. Mondello[1,2,3]
[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina, Polo Annunziata, viale Annunziata, 98168 – Messina, Italia
[2]Chromaleont s.r.l., c/o Università di Messina, Polo Annunziata, viale Annunziata, 98168 – Messina, Italia
[3]Università Campus Bio-medico di Roma, via Álvaro del Portillo, 21 - 00128 Roma, Italia

Isotope Ratio Mass Spectrometry (IRMS) is commonly recognized to be able to provide information about the geographical, chemical, and biological origins of substances. The ability to determine the source of substances stems from the relative isotopic abundances of the elements which comprise the material. By performing a separation prior to isotope ratio analysis, hyphenated techniques such as GC-C-IRMS, can provide isotopic analysis of a complex mixture, thereby providing additional information and higher discriminatory power. Since its introduction, the use of this analytical approach was not widespread due to a series of drawbacks related to chromatographic and isotopic issues. In fact, dead volumes due to the typical instrumental setup, requiring the combustion of the components followed by a drying step, often limit the separation efficiency, driving to an increased band broadening and peak asymmetry producing peak coelutions, thus falsify the measurements. Moreover, the reduced chromatographic performance increases the gas chromatographic isotope effect (or inverse isotopic effect) that generates GC peak not isotopically consistent because composed of lighter isotopes (^{12}C, ^{1}H and ^{16}O) that elute after the isotopomers containing heavier organic compounds because of their higher volatility. The present research deals with the development of an MDGC-MS/IRMS prototype characterized by the improved resolution capability of the heart-cut mode, exploiting two different GC stationary phases, and the simultaneous qMS and IRMS detection of the 2D chromatographic bands. The IRMS system was optimized in terms of dead volumes enabling to overcome the extra-column band broadening effect that usually affects the commercial systems. Different applications on food and flavour and fragrance samples are reported showing the enhanced performances of the prototype described.

A QUALITY-BY-DESIGN OPPROACH FOR THE DEVELOPMENT OF RP-HPLC METHODS FOR THE ANALYSIS OF PLANT SECONDARY METABOLYTES

D. Corradini[1], L. De Gara[2], I. Nicoletti[1], F. Orsini[2].
[1]National Research Council, Institute of Chemical Methodologies, Area della Ricerca di Roma 1, I-00015 Montelibretti, Rome, Italy
[2]University Campus Bio-Medico of Rome, Via Alvaro del Portillo 21, 00128 Rome, Italy.

Plant secondary metabolites are organic compounds produced besides the primary biosynthetic and metabolic routes that are believed to have a role in defense mechanisms, such as protection against biotic and abiotic stresses. Most of these phytochemicals, occurring as “non-nutritive” compounds in plant food, have found to play important roles in disease prevention and health-promoting effects, in addition to confer specific sensorial characteristics. Many others are biomolecules with biological activity employed in phytotherapeutic medicine. This communication discusses the results of our recent studies carried out to investigate a variety of factors that influence the chromatographic behavior of plant secondary metabolites, mainly phenolic compounds, with the purpose of developing novel RP-HPLC methods for the identification and quantification of bioactive compounds in plant extracts and foodstuff. We have investigated the dependence of retention behavior of a variety of biomolecules in RP-HPLC on the experimental parameters, such as flow rate, column length and internal diameter, dwell volume, temperature, isocratic and gradient elution mode, variation of the organic solvent concentration in gradient elution mode (gradient shape and duration). The influence of the considered parameters on the chromatographic behavior of the selected compounds has been evaluated in the framework of solvophobic theory [1], using a chromatographic modeling software that allows the development of RP-HPLC methods according to a Quality by Design (QbD) criteria, with the result of decreasing the number of experiments requested for method development and increasing flexibility in routine operations. Practical applications of the investigated approach to the analysis of secondary metabolites in samples extracted from edible plants and processed food are then discussed.

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DEVELOPMENT AND MULTIVARIATE OPTIMIZATION OF A MEPS-PTV-GC-MS/MS METHOD FOR ORGANOPHOSPHATE FLAME RETARDANTS ANALYSIS IN ENVIRONMENTAL AQUEOUS MATRICES

R. Elliani[1], A. Naccarato[2], G. Sindona[1], A. Tagarelli[1]
[1]Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via Pietro Bucci, Cubo 12/C – 87030 Arcavacata di Rende (CS)
[2]CNR-Istituto sull'Inquinamento Atmosferico, Divisione di Rende, Università della Calabria-Polifunzionale - 87036 Arcavacata di Rende (CS)

Organophosphate esters (OPEs) are chemical compounds frequently used as flame retardants and plasticizers in a variety of products, including plastics, foams, paints, textiles and furniture. Several OPEs have known or suspected adverse health effects such as toxicity. Moreover, OPEs are relatively stable toward biodegradation and are considered to be persistent pollutants.
The methods for the determination of OPEs in environmental samples generally involve an extraction step followed by a clean-up procedure before the instrumental analysis. OPEs extraction is normally performed by mean of liquid-liquid extraction or solid phase extraction. The features of these classical extraction approaches are further improved by the development of the microextraction techniques (METs), some of which were used for OPEs quantification. Microextraction by packed sorbent (MEPS) is a relatively recent microextraction technique that can be described as a miniaturized form of the solid phase extraction technique scaled down to the microliter level. This includes both the sample volume and the solvent usage with obvious advantages over the traditional sample preparation approaches in terms of cost, environment protection and applications [1].
The goal of the present work was to develop a rapid and versatile method for the analysis of OPEs by MEPS in environmental waters. Programmed temperature vaporization (PTV) was used to improve the method sensitivity and two liner types were tested. The MEPS and PTV working conditions were optimized by univariate and multivariate (Experimental design, DoE) approaches. Five solid packing materials were tested along with seven elution solvents. The results were compared and contrasted taking into account the extraction capability of the solid sorbent and the absence of analytes carryover. Tandem mass spectrometry in selected reaction monitoring (SRM) acquisition mode was used to obtain a high specific protocol capable of unequivocal and sensitive analyte quantification.

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DETERMINATION OF PERFLUORO-ALKYL ACIDS IN DIFFERENT WATER MATRICES BY MEANS OF DIRECT INJECTION LC-MS/MS ANALYSIS

M. Del Bubba[1], L. Ciofi[1], L. Renai[1], L. Checchini[1], A. Falai[2], D. Santianni[2], E. Coppini[3], D. Fibbi[3], S. Furlanetto[1]
[1]: Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Firenze
[2]: Publiacqua S.p.A., Via Villamagna 90/c, 50126 Firenze
[3]: G.I.D.A. S.p.A., Via Baciacavallo 36, 59100 Prato

Perfluoroalkyl acids (PFAAs) are characterized by high resistance to physical, chemical and biological degradation and a worldwide contamination of environmental matrices [1], including all water compartments, resulted from their extensive use for a wide range of industrial and commercial applications since the 1950s. In 2006, some regulatory restrictions have been promulgated both in United States and Europe in order to discipline the use of perfluorooctanesulphonic acid (PFOS) and perfluorooctanoic acid (PFOA), which were, until then, the most industrially employed chemicals among PFAAs.
The direct injection (DI) approach is an interesting alternative to extraction/clean-up procedures, such as solid phase extraction, since it allows to minimize the sample contamination due to its manipulation, to ensure high analytical throughput and to overcome any possible recovery issues related to the variety of physicochemical characteristic of these molecules (such as chain length and acidic moiety). However, the injection of relatively large volume of sample, together with the absence of the preconcentartion/purification steps, could translate into strong matrix effect which can negatively affect method accuracy and/or sensitivity.
This study aimed to evaluate the feasibility of the DI-LC-MS/MS approach for the analysis of selected carboxylic and sulphonic PFAAs in several water matrices (i.e. drinking water, groundwater, river water, lake water and wastewater). Method detection limits achieved in this study were found in the range 0.014-29 ng L^{-1}, resulting to be lower or comparable to those obtained with the same approach [2], or by means of SPE procedure [3]. For the first time, the presence of PFAAs in water samples - ranging from sub ng L^{-1} to tens of ng L^{-1} - has been determined in a number of rural, urban and industrial areas of Tuscany, Italy.
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ADVANCED OPERANDO X-RAY ANALYTICAL TECHNIQUES: CHARACTERIZATION OF NEW MATERIALS FOR SOLAR ENERGY CONVERSION

A. Giaccherini[1], W. Giurlani[1], B. Pasquini[1], F. Capolupo[1], R.A. Picca[2], R. Felici[3], F. Carlà[4], N. Cioffi[2], S. Furlanetto[1], A. Lavacchi[5], F. Di Benedetto[6] and M. Innocenti[1,5]
[1] Dipartimento di Chimica, Università Degli Studi di Firenze, Firenze
[2] Dipartimento di Chimica, Università Degli Studi di Bari "Aldo Moro", Bari
[3] SPIN – CNR, Roma, Italy
[4] ESRF, Grenoble, Cedex, France
[5] ICCOM – CNR, Firenze, Italy
[6] Dipartimento di Scienze della Terra, Università Degli Studi di Firenze, Firenze

Most of the mature technologies for energy conversion depend on critical raw materials, with a considerable environmental impact or involving energy intensive production techniques. These aspects have been recently emphasized by the European Union [1]. In this context, electrochemical techniques are of rising interest for the scientific community in order to tailor efficient process to exploit more and more available elements. Thus, new materials for energy conversion should have very favourable Full Life Cycle Assessment (FLCA). The deposition of new materials for solar energy conversion by means of Electrochemical Atomic Layer Deposition (E-ALD) is an interesting. Joining highly ordered products with the direct access to the final material, E-ALD has been proven to be very effective for the electrodeposition of ultra-thin films of semiconducting materials with band-gap suitable for solar energy conversion. Synchrotron Surface X-Ray Diffraction (SXRD) experiments were performed revealing some aspects of the growth mechanisms, to enable the design of solar devices based on these materials. Another promising application is the chemical to electrical energy conversion systems such as Alkaline Direct Alcohol Fuel Cells (ADAFC). Such devices provide electrical energy employing less critical catalyst than platinum and also interesting products for industrial application, i.e. acetates. To increase the durability and efficiency of these devices is crucial to devise the dynamics and reaction mechanisms at the electrochemical interface. In this context, FEXRAV (Fixed Energy X-ray Absorption Voltammetry) [2] constitutes a new promising technique, allowing operando X-ray absorption analysis during electrochemical processes and even in operative conditions.

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CHEMICAL VAPOR GENERATION ATOMIC SPECTROMETRY FOR CADMIUM DETERMINATION AT TRACE LEVEL: SOME RECENT DEVELOPMENTS

E. Pitzalis, D. Angelini, M.C. Mascherpa, A. D'Ulivo
Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici, via Moruzzi 1, – 56124 Pisa

Chemical Vapor Generation (CVG), one of the most useful derivatization techniques for trace and ultratrace analysis, coupled with atomic spectrometry or mass spectrometry, can be employed for quantification of Cd in water and aqueous matrices, but method optimization is complex, often employing additives[2]. CVG of Cd has been investigated by continuous flow reaction system coupled either with quartz tube (QTA) or mini diffusion flame (MDF) and AAS or with ICP-OES. As a reductant, hydroxytrihydriborate(III), $[BH_3OH]^-$, was synthesized on-line by quenching the acid hydrolysis of BH_4^- by NaOH.
With QTA-AAS, in the range 1-5 μg L-1 Cd, the use of BH_3OH^- in alkaline conditions increases the sensitivity of about a factor 2.2 with respect to BH_4^-, indicating an improved generation efficiency. Dissolved oxygen has been proved to severely interfere, in the liquid phase, using both BH_4^- and BH_3OH^-. The use of BH_3OH^- under oxygen free conditions resulted about 13 fold improved LODs (about 10 ng L-1, 3s). Signal enhancement in the absence of oxygen varies with generation condition, being lower with ICP-OES and MDF/AAS at higher Cd levels.
Tests at increasing temperatures with QTA showed that both molecular Cd species and free Cd atoms are generated. More Cd free atoms were generated in the absence of dissolved oxygen, in both THB or QFR systems.
Calibration curves obtained either by reduction with BH_4^- or BH_3OH^- are affected by rollover at Cd concentration of 50-100 μg L^{-1}, depending on reaction conditions, with double peaks formation, that can be addressed to self interference effect due to dispersed solid phase formed by Cd atoms aggregation.
In the QFR mode, Ni(II), Co(II) and Fe(III) strongly decrease sensitivity at 10 mg L^{-1} in the sample solution while 50 μg L^{-1} Cu(II) produces the same effect, probably due to the high strength of the reductant. The well known thiourea/Ni modifier had no effect in controlling the interferences by either addition to the sample solution or online addition to the reaction mixture. On the contrary, while 10 μg L^{-1} Ni acts as a catalyst in the absence of thiourea, thiourea severely decreases the signal over 0.1 % m/v.

TRIBOLOGICALLY-INDUCED STRUCTURAL EVOLUTION OF SILICON OXIDE-DOPED HYDROGENATED CARBON: A SURFACE-ANALYTICAL INVESTIGATION

F. Mangolini[1], K.D. Koshigan[2], M.H. Van Benthem[3], J.A. Ohlhausen[3], J.B. McClimon[4], J. Hilbert[5], J.R. Lukes[5], J. Fontaine[2], R.W. Carpick[5]
[1] Institute of Functional Surfaces, School of Mechanical Engineering, University of Leeds, Leeds, LS2 9JT, UK
[2] Laboratoire de Tribologie et Dynamique des Systèmes, Ecole Centrale de Lyon, 69134, Ecully cedex, France
[3] Sandia National Laboratories, Albuquerque, New Mexico 87185, USA
[4] Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA
[5] Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, USA

Silicon oxide-doped hydrogenated amorphous carbon (a-C:H:Si:O) coatings are amorphous thin-film materials composed of hydrogenated amorphous carbon (a-C:H), doped with silicon and oxygen. a-C:H:Si:O films overcome the most critical Achilles' heels of a-C:H films, namely their high friction and wear at high humidity, high residual stresses, susceptibility to oxidative degradation, and limited thermal stability. Thus, a-C:H:Si:O materials are in use, or being considered for use, as solid lubricants for a number of applications, including aerospace, microelectronics, and hard disks.
While the tribological properties of these films have been studied quite extensively in different environments (from dry to humid atmospheres) [1], only a few studies have focused on the mechanisms by which their excellent tribological performance is achieved. This work aims to develop fundamental understanding of structural transformations occurring in a-C:H:Si:O when sliding against steel under different environmental conditions (from high vacuum (HV) to controlled hydrogen and oxygen pressures).
Tribological tests were performed using a pin-on-flat configuration, where a steel pin was slid on an a-C:H:Si:O surface. The results revealed a strong environmental dependence of the tribological performance of a-C:H:Si:O: upon increasing the oxygen (hydrogen) pressure from 10 mbar to 1000 mbar, the coefficient of friction increased (decreased). The characterization by imaging near edge X-ray absorption fine structure (NEXAFS) spectroscopy of a-C:H:Si:O after the tribological tests revealed that, independent of the gas, a conversion from sp^3- to sp^2-bonded (disordered) C-C bonds occurred. The NEXAFS data also indicated that, while sliding in oxygen, the dissociative reaction of oxygen molecules with strained sp^2 C-C bonds resulted in the formation of carbonyl groups. This could explain the increase of friction with oxygen pressure by either increasing the shear strength of the material generated at the sliding interface or forming ether linkages across the

interface. Similarly, we propose that when sliding in hydrogen, the newly-generated sp^2 strained carbon layer reacts with hydrogen molecules. This reaction, which leaves a hydrogen-passivated layer, results in the generation of a hydrogenated amorphous carbon material with a low shear strength at the sliding interface, thus leading to a decrease in friction with gas pressure.
These results, highlighting that surface chemical processes control the tribological response of a-C:H:Si:O and that good tribological performance is critically dependent on the environment, add significantly to the understanding of the tribology of amorphous carbon coatings.

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SYNTHESIS OF NANOANTIMICROBIALS BY LASER ABLATION IN LIQUIDS AND THEIR APPLICATION TO FOOD PACKAGING

M.C. Sportelli[1,2], A. Ancona[2], R.A. Picca[1], A. Volpe[2,3], P.M. Lugarà[2,3], N. Cioffi[1]
[1]Chemistry Department, University of Bari, V. Orabona, 4-70126 Bari, Italy
[2]IFN-CNR, Physics Department, University of Bari, V. Orabona, 4-70126 Bari, Italy
[3]Physics Department, University of Bari, V. Orabona, 4-70126 Bari, Italy

Laser-generated metal nanoparticles (NPs) are a novel class of bioactive agents, providing enhanced and synergistic efficiency in the prevention of biocontamination in several application fields, from food packaging to containment of nosocomial infections [1]. Designing bioactive materials, with controlled metal ion release, exerting significant bioactivity and low cytotoxicity, is an important challenge for scientists.
Based on our previous paper on CS-stabilized CuNPs [2], in this work we propose the femtosecond laser synthesis in the two-step of Ag/Cu bi-component colloids. Bimetal NPs offer unique catalytic, electrochemical and optical properties, compared to monometal NPs [3,4]. Moreover, the case of Cu/Ag hybrid structures is particularly appealing, due to the combination of the antimicrobial activity of both metals [1]. On the other hand, such hybrid nanocolloids pose some critical issues to the analytical chemist approaching their characterization in terms of stability/reactivity after preparation, especially when techniques (e.g. TEM, XPS) involving the use of highly focused beams (X-rays, electrons) are considered.
Regarding the synthesis, the Cu and Ag solid target were immersed into aqueous or organic solutions, eventually containing some polymeric stabilizers (e.g. chitosan - CS) [2]. We used a novel flow-through experimental setup, which removes fs-laser-synthetized NPs reducing their interactions with incident beam. Ag and Cu targets were alternatively selected as first ablated material, followed by the ablation of the second one, either in aqueous and organic solution. Bimetal NPs were characterized by transmission electron microscopy (TEM), UV-Vis, and X-ray photoelectron spectroscopy (XPS), to evaluate their structure, morphology and chemical composition.

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RECENT APPLICATIONS OF PLASMONIC NANOMATERIALS AND THEIR COMPOSITES: FROM LOCALIZED SURFACE PLASMON RESONANCE (LSPR) TO COLORIMETRIC DETECTION FOR BIOANALYSIS

S. Scarano[1], M. Bonini[1], M.G. Manera[2], A. Colombelli[2], R. Rella[2], and M. Minunni[1]
[1]Department of Chemistry 'Ugo Schiff' and CSGI, University of Florence, via della Lastruccia 3-13, Sesto Fiorentino, 50019, Firenze, Italy.
[2]CNR-IMM-Institute for Microelectronic and Microsystems, Unit of Lecce, Via per Monteroni, 73100 Lecce, Italy

Plasmonic nanomaterials (PNs) display exciting optical properties and tunability, and during last decade their use has been pushed toward innovative and creative applications, combining the design of cheap and smart detection strategies to impressive analytical performances. Nowadays there is a huge availability of metallic/semi-metallic nanostructures of different figure of merit (FOM) on the market. Alternatively, their simple fabrication can be achieved by home-made synthesis, via metal salts reduction, or by nanolithography-based techniques. As consequence, a plethora of optical substrates for sensitive and selective spectrophotometric measurements based on Localized Surface Plasmon Resonance (LSPR) is presently applied to several (bio)analytical research fields (1). PNs can be optically interrogated through collective oscillations of localized plasmons, which result very sensitive to perturbations taking place at the nanoparticles/medium interface. These events can be hence transformed into wavelength shifts of the absorption band, as well as in a color change of the nanoparticles solution. Therefore, LSPR of metal nanoparticles can be easily observed by measuring changes in their extinction spectrum, both in terms of wavelength shift and absorbance intensity. For gold and silver nanoparticles (mNPs), their plasmon absorption bands are generally located in the visible region, making them particularly suitable for many (bio)sensing applications. On the basis of readout, there are two LSPR sensing strategies, including absorption band shift and colorimetric sensing. In this presentation, recent applications based on metallic nanoparticles in solution or supported on polymeric layers are reported for different target analytes, from small molecules to large proteins. In solution, metallic NPs can be exploited both via aggregation induction and their tailored formation from metal ions under the reducing pressure of specific analytes, giving punctual information about their concentration and properties. Regarding the last approach, some on going work on glyco-nanoparticles formation under the reducing action of different sugars is here presented, exploiting gold(III) and silver(I).
Finally, several polymers have recently demonstrated to be very interesting substrates with intrinsic reducing capability leading to the controlled *in situ*

growth of mNPs for optical purposes (4-6). These composite substrates allow for the realization of LSPR-based (bio)assays displaying high versatility, sensitivity and specificity, and preliminary results in this sense will be presented.

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AN XPS STUDY OF ELECTROCHEMICALLY DEPOSITED SULPHIDE SEMICONDUCTORS FOR THIN FILM PHOTOVOLTAICS

R.A. Picca[1], A. Giaccherini[2], F. Di Benedetto[3], M. Innocenti[2], N. Cioffi[1]
[1]Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via E. Orabona, 4 – 70126 Bari
[2]Dipartimento di Chimica, Università degli Studi di Firenze, Via della Lastruccia 3 – 50019 Sesto Fiorentino (FI)
[3]Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via La Pira, 4 – 50121 Firenze

Semiconducting sulphides based on low-cost, abundant, non-toxic elements (e.g. Cu, Zn, Fe) are considered appealing materials to overcome Silicon and CI(G)S (copper-indium-gallium-sulphur) technologies in the field of thin film photovoltaics (PV). Ternary (e.g. $Cu_xSn_yS_z$) and quaternary (e.g. kesterite, Cu_2ZnSnS_4 or CZTS) chalcogenide-like materials may be prepared according to different methodologies [1–3], mainly based on vacuum processes. On the other hand, a more versatile approach, carried out at ambient pressure and room temperature, is the Electrochemical Atomic Layer Deposition (E-ALD) [4] for the growth of multinary sulphide thin films on conducting substrates (e.g. Ag(111)) [5, 6]. The alternating underpotential deposition of the metal and non-metal components as monolayers allows preparing sulphides of different stoichiometry and thickness, hence tuning the final PV properties of the as-prepared thin films. Due to the intrinsic nature of these materials, X-ray Photoelectron Spectroscopy (XPS) can be particularly useful not only to investigate their surface chemical composition, but also to discriminate different chemical environments associated to the identified elements. Recently, we have demonstrated the feasibility of this approach, especially when angle-resolved mode XPS is applied [6]. Here we present the XPS study carried out on both binary and ternary sulphides. It will be also shown how XPS can be correlated to other morphological (Scanning Electron Microscopy) and spectroscopic investigations (e.g. in situ Surface X Ray Diffraction with Synchrotron Radiation).

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FLAT BIMETALLIC MICRO- AND NANO-PATTERNS FOR CALIBRATION OF SURFACE ANALYSIS INSTRUMENTS

C. Passiu[1], A. Rossi[1,2], W. Unger[3], N. D. Spencer[1]
[1]Laboratory for Surface Science and Technology, Department of Materials, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland
[2]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Cittadella Universitaria di Monserrato, I-09100 Cagliari
[3]BAM Federal Institute for Materials Research and Testing Unter den Eichen 87, 12205 Berlin, Germany

The determination of properties such as lateral resolution, analysed area and image sharpness, as defined by ISO for surface spectroscopic techniques [1], is important for instrumental calibration. The reference materials currently used for measuring such properties usually consist of bi-material surfaces or metal-vacuum edges. In both cases the topography of the samples has an influence on the measured resolution. In order to avoid any topographic influence, the component materials should be present on an atomically flat surface. Flat samples have been already produced for determination of lateral resolution in SIMS instruments [2]. We propose an approach for obtaining flat micro- and nano-patterned surfaces where a metal is embedded in another. The novelty of this approach resides in the present of different calibration designs on the same sample, specifically thought for calibration of XPS, ToF-SIMS and AES.

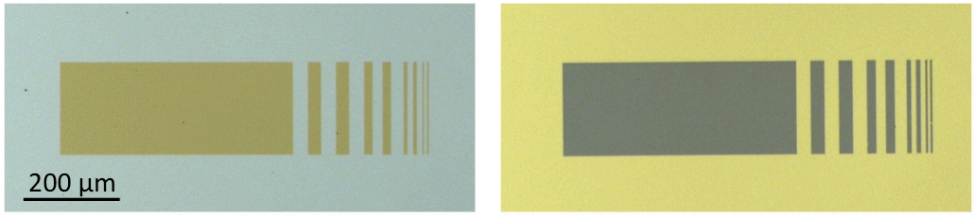

Figure 1: optical microscopy images of a section of the surface of samples for XPS calibration. Left: Au patterns in Ag; right: Ti patterns in Au. The grating of stripes is dedicated to the determination of lateral resolution.

The preparation procedure consists in designing the structure on a silicon wafer by photolithography (micro-patterns) or electron-beam lithography (nano-patterns), then producing a flat surface by stripping away the wafer template. Gratings of stripes are designed for lateral resolution and image sharpness measurements, while circles of different sizes can be used for determining the analyzed area.

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MULTIVARIATE INVESTIGATION OF STEROIDOMIC PROFILES FOR CANCER DIAGNOSIS, PHYSIOLOGICAL ALTERATIONS RECOGNITION AND DOPING CONTROL

E. Alladio[1,2], E. Amante[1,2], C. Bozzolino[1,2], E. Gerace[2], A. Salomone[2], M. Vincenti[1,2]
[1]Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 7, 10125 Torino, Italy.
[2]Centro Regionale Antidoping "A. Bertinaria", Regione Gonzole 10/1, 10043 Orbassano, Torino, Italy.

The Technical Document TD2014EAAS was drafted by the World Anti-Doping Agency (WADA) in order to fight the spread of endogenous anabolic androgenic steroids (EAAS) misuse in several sport disciplines[1]. In particular, adoption of the so-called Athlete Biological Passport (ABP) – Steroidal Module allowed control laboratories to identify anomalous EAAS concentrations within the athletes' physiological urinary steroidal profile. Gas chromatography combined with mass spectrometry was utilized to develop a Multivariate Data Analysis model combining Principal Component Analysis and Hotelling's T^2 techniques to identify anomalous steroidal profiles through the simultaneous evaluation of all EAAS markers specified in TD2016EAAS [2]. An extended urinary steroidal profile has subsequently been utilized to discriminate subjects suffering from prostatic pathologies (hypertrophy or carcinoma) from healthy individuals. Moreover, the side-effects of some pharmaceutical drugs (statins) on the physiological hormone balance were studied with the same approach. Eighteen EAAS and their ratios have been included in the analytical-statistical method. Feature selection strategies using Genetic Algorithms method allowed to identify different sets of discriminant variables that were utilized to build classification models involving Partial Least Squares – Discriminant Analysis and multivariate likelihood ratio approaches. Three classification models have been developed, providing discrimination between: (i) statins-user patients from non-users, (ii) subjects affected by prostatic diseases from healthy individuals, (iii) individuals suffering from benign prostatic hyperplasia from subjects suffering from prostatic carcinoma.

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ALLOSTERIC DNA NANOSWITCHES FOR CONTROLLED RELEASE OF A MOLECULAR CARGO TRIGGERED BY BIOLOGICAL INPUTS

M. Rossetti, S. Ranallo, A. Idili, G. Palleschi, A. Porchetta, F. Ricci
Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma "Tor Vergata", Via della Ricerca Scientifica 1 – 00133 Roma

In Nature the activity of many functional biomolecules is controlled, turned-on or shut-down, by means of allostery, a mechanism through which the binding of an effector at one site of the functional protein causes a conformational change that affects (activate or inhibit) its functionality. Furthermore, allostery is also strongly involved in processes that allow the transport of molecular cargoes across the cell. Because of the versatility of the allosteric mechanism to control different biochemical functions, the possibility to recreate in-vitro allosterically-regulated mechanisms represent one of the main challenges in the field of synthetic biology and biotechnology for the development of "smart" biomaterials,[1] novel theranostic tools,[2] and drug-release devices with controlled features.[3]
Here we demonstrate the rational design of a new class of DNA-based nanoswitches allosterically regulated by specific biological targets, antibodies and transcription factors, able to release a molecular cargo (i.e. doxorubicin) in a controlled fashion. In our first model system we rationally designed a stem-loop DNA nanoswitch that adopts two mutually exclusive conformations: a "load" conformation containing a doxorubicin-intercalating domain and a "release" conformation containing a duplex portion recognized by a specific transcription-factor. The binding of the transcription factor pushes this conformational equilibrium towards the "release" state thus leading to the doxorubicin's release from the nanoswitch. In our second model system we designed a similar stem-loop DNA nanoswitch whose conformational change and subsequent doxorubicin's release can be triggered by a specific antibody. By taking inspiration from naturally-occurring proteins, our approach augments the current tool kit of smart drug delivery systems regulated by different biological inputs.

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PERCUTANEOUS ABSORPTION OF FLAME RETARDANTS

M. Crosera[1], M. Venier[2], J. Guo[2], A. Phillips[3], H. Stapleton[3], F. Filon Larese[4], E. Baracchini[1], G. Adami[1]
[1] Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via L .Giorgieri, 1 – 34127 Trieste
[2] School of Public and Environmental Affairs, Indiana University, 702 N. Walnut Grove avenue, Bloomington, Indiana 47405
[3] Nicholas School of the Environment, Duke University, 450 Research Drive, Durham, NC 27708-0328
[4] UCO Medicina del Lavoro, Dipartimento Universitario Clinico di Scienze Mediche, Chirurgiche e della Salute, Università di Trieste, Via della Pietà 19 – 34129 Trieste

Flame retardants (FRs) are chemicals added to a wide variety of products to meet flammability codes. Halogenated FRs have been widely used since the 1970s. Because most are additives that are not chemically bonded, halogenated FRs migrate from materials into the surrounding environment, thereby creating opportunities for human exposure. 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB) and bis(2-ethylhexyl)-tetrabromophthalate (BEHTBP) are two main replacements of PBDEs, which were withdrawn from the market in 2004. Recent studies suggested that dermal uptake of PBDEs from dust could contribute substantially to the overall exposure, up to 40% in children and up to 20% in adults [1].
The *ex vivo* dermal absorption of EHTBB and BEHTBP and their metabolites has been evaluated using Franz diffusion cells [2]. The experiment was performed with human cryopreserved skin from 2 donors. 9 cells were filled with 1 mL of a solution obtained dissolving 1.0 g of the commercial mixture BZ-54 in 10 ml of ethanol. Two blanks were collected.
Due to the low water solubility of these compounds, a physiological solution (pH 7.35) with 8% bovine serum albumin was used as the receptor fluid. For this preliminary study, a 24 hour cumulative absorption was evaluated. After 24 hours, the whole volume of the receptor fluid, the donor solution and the exposed tissue of each cell were collected. After the extraction and clean-up procedures, parent compounds were analysed using gas chromatograph mass spectrometry (GC-MS) and the metabolites using liquid chromatography mass spectrometry (LC-MS-MS)
The presence of both chemicals in the skin and in the receiving fluid suggests that they are absorbed through the skin and that the skin acts as reservoir. Different ratios of parent/metabolites in the three phases might indicate metabolism is occurring in the skin.

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SAMPLING AND CHARACTERIZATION OF SUBMICRON AND ULTRAFINE PARTICLES: AN INTEGRATED APPROACH IN THE EXPOSURE ASSESSMENT DURING ALUMINIUM WELDING PROCESS

E. Baracchini[1], A. Prodi[2], M. Crosera[1], P. Canton[3], F. Larese Filon[2] and G. Adami[1]
[1] Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via Giorgieri 1- 34127 Trieste
[2] UCO Medicina del Lavoro, Dipartimento Universitario Clinico di Scienze Mediche Chirurgiche e della Salute, Università di Trieste, Via della Pietà 19– 34129 Trieste
[3]Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155-30170 Venezia Mestre

In the working environment, different kinds of sources of ultrafine particles (UFPs) can be found. Several studies are ongoing in the field of nanotoxicology but there are still important gaps in the study of exposure to UFPs in real occupational contexts. At present time, there are no existing standardized methods for either assessing or monitoring the occupational exposure to UFPs that may follow several routes: inhalation, cutaneous contact and gastroenteric pathway.
In this study an integrated approach was used to assess the exposure to submicron and UFPs of workers during aluminium welding. In order to evaluate the presence of airborne particles the following instruments were used: i) a miniature diffusion size classifier (DiscMini Matter Aerosol) to measure the number concentration and mean diameter of particles in the range 10-300 nm near and far from the emission source during a work shift;
ii) a personal cyclone sampler for respirable dust both for ICP-AES analysis of particles collected on 0.45 μm cellulose filter, and morphological and chemical characterization of particles directly collected on TEM grids. Carbon tabs were applied on surfaces in the welding position and over the gloves of workers and analysed by means of SEM-EDS to evaluate the deposition of particles. Tape stripping of welders' skin was performed and the samples were analysed by means of ICP-AES for a quantitative determination in order to evaluate cutaneous contamination.
The results of the analyses performed on respirable dust samples showed that the aluminium concentrations were about three orders of magnitude lower than the ACGIH limit for respirable aluminium (1 mg/m3 air sampled). Nevertheless, the mean number concentration of particles in the range 10-300 nm near the emission source was 50000 pt/cm3, with peaks an order of magnitude higher, and the mean diameter was 35 nm (far from the emission source: about 15000 pt/cm3; mean diameter 50 nm). Furthermore, TEM-EDS and SEM-EDS investigations, respectively on airborne and deposited

particles, revealed the presence of agglomerates of nanoparticles containing aluminium. In conclusion, an integrated approach which takes into account air sampling, skin and surfaces contamination should be recommended to assess the workers' exposure to UFPs.

Poster

EFFECT OF DIFFERENT ROOTSTOCKS ON ELEMENT UPTAKE

M. Radaelli[1], E. Scalabrin[1], G. Rizzato[1], M. Gardiman[2], G. Capodaglio[1]
[1]Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca Foscari Venezia, Via Torino , 155 – 30172 Mestre - Venezia
[2] CREA - Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria, Centro di ricerca per la Viticoltura,Viale 28 Aprile, 26-31015 Conegliano – Treviso

The research results of the last decades showed that the industrial and the inadequate agricultural activity may increase the concentration of potentially toxic elements in soil.
The grape rootstock is a filter system in the grapevine, which may modulate trace elements transfer from soil to the grape berry.
Therefore it is very important, in the wine sector, to understand which rootstock should be applied, to minimize uptake of the toxic elements of the soil, in order to maintain sufficiently low the concentrations in the fruits.
The choice of the rootstock is very important, not only as regards the up-take of potentially harmful elements, but also because the nature and characteristics of a rootstock are able to influence the organoleptic properties of wine. Indeed rootstock varieties differently affect fruiting, rate of growth, yield and fruit quality [1].
In this research 60 germoplasm accessions including different rootstocks commonly used (eg. Kober 5 BB, 1103 Paulsen, 110 Richter), other hybrids rarely used (eg. 216-3 Castel, 1616 Couderc) and *Vitis* species used as parental to form hybrid rootstocks (eg. V. cinerea, V. berlandieri) were studied. After tests were carried out to verify the homogeneity of land cultivation, the concentration of some trace elements and nutrients were examined in rootstock leaves to define the different metal up-take mechanisms,
Simultaneous determination of Al, As, Ba, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Mg, Mn, Na, Pb, Rb, Sr, V and Zn was carried out by ICP-MS equipped with a collision/reaction cell (ICPORS-MS). In order to reduce the uncertainty of the experimental results as in a previous study [2], the methodology was optimised by testing the grinding, homogenisation, digestion and analysis procedures.

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DETERMINATION OF BIOLOGICAL ACTIVE COMPOUNDS IN FOOD MATRICES: COMPARISON OF SAMPLE PRETREATMENT PROCEDURES FOR THE EXTRACTION OF BETAINE *FROM CHENOPODIACEE* ROOTS AND DETERMINATION BY HPLC-MS/MS

L. Rivoira[1], M. Szultka-Młyńska[2], S. Studzińska[2], B. Buszewski[2], M. C. Bruzzoniti[1]
[1]Department of Chemistry, University of Torino, Torino, Italy
[2]Department of Environmental Chemistry and Bioanalytics, Nicolaus Copernicus University, Torun, Poland

Betaine is an amino acid widely present in animals and plants, such as beetroots, where polar betaine is accumulated in response to water stresses. Betaine takes part in the protection of cells, proteins and enzymes from environmental stress and participates in the methionine cycle in human liver and kidneys. The most important feature is however betaine biological relevance in reducing cancer development.
Despite these biological effects of betaine, just few analytical methods for its extraction from highly accumulating beetroots are by far reported; these approaches are mainly based on solid phase extraction (SPE) that however does not provide quantitative recoveries.
The aim of this work was the development of a new, quick and effective procedure for the isolation and determination of betaine from two different varieties of *Beta Vulgaris* (Red and Gold). For the first time an accelerated solvent extraction (ASE) with methanol was coupled with solid phase extraction on silica cartridge to isolate betaine from interfering species co-extracted. Additionally, the performance of a micro extraction by packed sorbent (MEPS) after the ASE extraction was also studied. A modified QuEChERS procedure was finally tested in order to join the extraction and clean-up stages in a unique analytical protocol. Qualitative and quantitative analyses were performed with the use of LC-MS/MS (negative ESI, MRM mode) after separation by hydrophilic interaction liquid chromatography (HILIC). The mass spectrometry parameters were optimized by means of a Central Composite Design. Recoveries of betaine from beetroots were about 97% (RSD<6%) with the use of ASE coupled to SPE. The total content of betaine in extracts of various part of plants (juice, peel, root) have been determined and compared.

BIOACTIVE PEPTIDES IN DONKEY MILK: IDENTIFICATION BY MULTIDIMENSIONAL CHROMATOGRAPHY AND NANO-HPLC-MASS SPECTROMETRY

C. Cavaliere, F. Ferraris, G. La Barbera, S. Piovesana, R. Zenezini Chiozzi, A. Laganà
Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", piazzale Aldo Moro 5 – 00185 Roma

Donkey milk is a valuable product for the food industry, and nowadays it is considered a "pharmafood" for its nutritional values [1]. It strongly resembles human milk (similar amounts of lactose and minerals, and similar fatty acid and protein profile), therefore it is considered the best infant food, especially in case of cow milk allergy; moreover, interesting biological activities were ascribed to donkey milk.
The characterization and discovery of novel bioactive proteins or peptides, generated from endogenous proteases, microbial fermentation, thermal treatment or storage, could be significant because they could be used as bioactive compounds in functional foods.
In this work, a combination of consecutive chromatographic separations, including polymeric-based reversed phase liquid chromatography (RP-LC) and hydrophilic interaction chromatography (HILIC), was used to to reduce sample complexity and purify endogenous peptides in donkey milk. Bioactivity assays were performed on individual fractions, and the fractions obtained from the second chromatographic dimension with the highest antioxidant and angiotensin-converting-enzyme (ACE) inhibitory activites were further analyzed by nanoRP-LC coupled with a hybrid linear ion trap-Orbitrap mass spectrometer for peptide sequencing, in order to restrict the number of possible bioactive sequences. In silico analysis using PeptideRanker was then employed to ascribe a bioactivity score to the identified peptides and match sequences to known bioactive peptides, in order to select candidates for chemical synthesis. On the basis on the composition and the probability as calculated by PeptideRanker algorithm, five peptides were selected and synthesized. The synthetized peptides were compared to the natural occurring ones checking their retention times and fragmentation patterns in donkey milk alone and donkey milk with spike-in peptides. Pure peptide standards were finally in-vitro tested for the specific bioactivity. In this way two novel endogenous anti-oxidative, namely EWFTFLKEAGQGAKDMWR, GQGAKDMWR, and two ACE-inhibitory peptides, namely REWFTFLK and MPFLKSPIVPF, were successfully validated from donkey milk.

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EXPLOITING THE OXITEST REACTOR IN THE FIELD OF FOOD PACKAGING

A. Cavazza[1], C. Bignardi[1], C. Laganà[1], P. Salvadeo[1], S. Corti[2], C. Mancinelli[2], C. Corradini[1]
[1]Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze, 17/A – 43124 Parma
[2] Velp Scientifica srl, Via Stazione, 16 – 20865 Usmate MB

Oxitest (VELP Scientifica, Italy) is a reactor based on the use of high temperature and over-pressure of oxygen that allows to easily measure a sample oxidative stability by accelerating the oxidation process. It has been shown to be a very useful tool for testing many types of food.
In this work, the use of Oxitest in the field of food packaging was explored, testing its usefulness for the assessment of the shelf-life of food stored in glass and in metallic cans, and for the evaluation of the suitability of new proposed packaging materials.
Glass and metals are at present the most popular materials for packaging of canned products preserved in oil. However, plastic materials are lately being used for applications once restricted to metals and glass, allowing weight saving and design versatility benefits. In this context, an important step to take into account during the production process is the resistance to autoclaving, a sterilization process at high pressure and temperature. Indeed an alteration of the properties of the packaging material would affect the shelf-life of the food product to be stored.
Two polypropylene-based materials equipped with oxygen barrier were selected. The oxidative stability of an olive oil sample stored in the two different packaging materials was tested before and after autoclaving. The one showing higher stability was then subjected to an accelerated ageing process in a climate chamber in order to evaluate the effect of a shelf-life greater than 6 months at room temperature.
Canned tuna fish in olive oil was chosen as food model to measure oxidative stability along shelf-life. Samples stored for different periods were submitted to analysis. Surprisingly, results showed a progressive increase of tuna fish oxidative stability with time, accompanied by a parallel decrease of the olive oil stability. It can be supposed that the antioxidant compounds occurring in olive oil exert a protective effect on the soaked tuna fish fillets. An interesting conclusion is that tuna fillet shelf-life is prolonged after its storage in olive oil, and even increases its quality, in terms of oxidative stability, with time.

COMPARISON BETWEEN PHARMACOKINETICS AND METABOLISM OF BERBERINE AND BERBERRUBINE IN A RAT MODEL BY MEANS OF LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY.

E. Porru[1], P. Franco[1], S. Spinozzi[1], M. Cont[2], M. Roberti[3], C. Caliceti[1], A. Roda[1]
[1]Dipartimento di Chimica, Università di Bologna, Via Selmi, 2 – 40126 Bologna
[2]INBB, Istituto Nazionale Biostrutture e Biosistemi, Roma, Viale delle Medaglie d'Oro, 305 - 00136 Roma
[3]Dipartimento di Farmacia e Biotecnologie, Università di Bologna, Via Belmeloro, 6 – 40126 Bologna

Berberine (BBR) is one of the major nutraceutical components of *Berberis* plants. It has been clinically applied for decades because of its significant beneficial properties, above all its lipid-lowering effect [1]. Scientific studies showed that this activity is correlated to the BBR capacity of increasing low-density lipoprotein receptor (LDLR) expression [2]. Considering the low BBR bioavailability, it has been proposed that its primary metabolites are the real *in vivo* active form and the main responsible of its health benefits. Among these metabolites, Berberrubine (M1) showed the highest up-regulatory effect on LDLR mRNA expression and the highest bioavailability [3]. Basing on these considerations, a comparison study of pharmacokinetics and metabolism of M1 and BBR in rats has been performed. For this purpose, a suitable HPLC-ES-MS/MS method was developed and validated, according to ICH guidelines, to measure BBR, M1 and their metabolites in different biological matrices such as plasma, liver, kidney, intestinal contents, urine and stools.
Good accuracy (bias% < 10%) and precision (CV% < 10%), very low detection and quantification limits (0.1–0.5 ng/mL) were obtained, ensuring sufficient sensitivity and selectivity for this kind of study. The optimized extraction procedures afforded recoveries higher than 90%, while matrix effects (M.E.) were negligible (M.E.%<15%). The developed method resulted to be suitable for pharmacokinetics and metabolism studies, affording total BBR and M1 recoveries 24 hours after administration of, respectively, 82% and 76% of the dose. Results showed an higher bioavailability of M1 after its direct administration respect to BBR, putting in evidence how M1 could be a potent tool as phytotherapic agent for the treatment of dislipidemic diseases.

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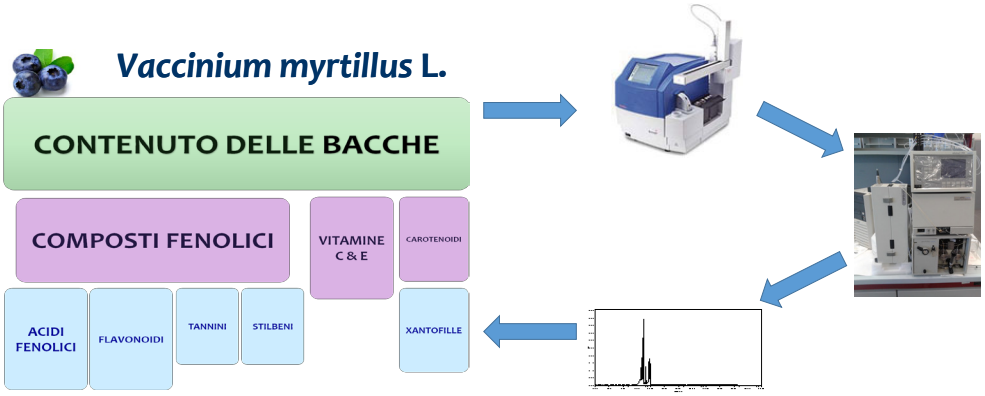
MICROWAVE-ASSISTED EXTRACTION, HPLC-PDA ANALYSIS AND ACTIVITIES ON CARBONIC ANHYDRASE ISOFORMS OF BLUEBERRY ITALIAN CULTIVARS

S. Carradori[1], M. Locatelli[1], G. Bellagamba[1], G. Macedonio[1], L. Mannina[2,3], F. Iannace[1], A. Mollica[1], C.T. Supuran[4]
[1]Department of Pharmacy, "G. D'Annunzio" University of Chieti-Pescara, Via dei Vestini 31, 66100 Chieti, Italy. E-mail: marcello.locatelli@unich.it
[2]Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza University of Rome, P.le A. Moro 5, 00185 Rome, Italy
[3]Institute of Chemical Methodologies, Magnetic Resonance Laboratory "Annalaura Segre", National Research Council, Monterotondo, Rome, Italy
[4]Laboratorio di Chimica Bioinorganica, Università degli Studi di Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino (Florence), Italy

The multicomponent pattern and biological evaluation of plant-derived material are indispensable for pharmaceutical field, in the food quality control procedures and into all plant-based products. The quantitative content of biologically active compounds (anthocyanins and chlorogenic acid) after Microwave-assisted extraction (MAE), using validated HPLC-PDA method and routinely instrument configuration, and their putative impact on the pharmacological results (selective carbonic anhydrase isoforms inhibition) allowed us to better characterization the blueberry extracts of fourteen different Italian cultivars [1]. Indeed, due to the occurrence of specific nutrients, valuable effects related to their intake are observed on human health and studies on this topic play a central role for new drug development process.



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CHEMICAL FINGERPRINT AND BIOLOGICAL ACTIVITIES OF SEVEN *ASPHODELINE* TAXA: POTENTIAL SOURCES OF NATURAL-FUNCTIONAL INGREDIENTS FOR BIOACTIVE FORMULATIONS

G. Bellagamba[1], E. De Luca[1], M. Locatelli[1], G. Zengin[2], L. Menghini[1], R. Cifelli[1], A. Uysal[3], A. Aktumsek[2], I. Lazarova[4], S. Carradori[1]
[1]University "G. d'Annunzio" Chieti-Pescara, Department of Pharmacy, 66100, Chieti-Italy; E-mail: marcello.locatelli@unich.it
[2]Selcuk University, Science Faculty, Department of Biology, Konya-Turkey
[3]Deparment of Medicinal Laboratory, Vocational School of Health Services, Selcuk University, Turkey
[4]Department of Chemistry, Faculty of Pharmacy, Medical University of Sofia, Bulgaria

The current study [1] was carried out to evaluate chemical fingerprint, biological and enzymatic activities of seven *Asphodeline* taxa root extracts.
The extracts were briefly characterized for free anthraquinones and phenolics to obtain a specific chemical fingerprint useful for quality control. Antioxidant properties were determined by different assays including free radical scavenging, reducing power, phosphomolybdenum and metal chelating assays. Ames assay was performed to evaluate mutagenic/antimutagenic properties. Enzyme inhibitory activities were tested against cholinesterase, tyrosinase, α-amylase and α-glucosidase. Chrysophanol were detected as the predominant anthraquinone. The major component was physcione. Between phenolics, gallic, vanillic and benzoic acid are the most representative compounds. Total phenolics and flavonoids content ranged from 18.61-34.03 mgGAEs/g extract and 10.33-27.69 mgREs/g extract, respectively. The activities of ADG, ADO, and ATT were noticeable than other extracts.
From the herein reported results, *Asphodeline* could be valuable for the production of bioactive products or food supplements, cosmetic and pharmaceutical industries.

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DETERMINATION OF PHOSPHATIDYLCHOLINE USING IMMOBILIZED ENZYME REACTOR

A. Apriceno, G. Esposito, A.M. Girelli
Dipartimento di Chimica, Università La Sapienza, P.le A.Moro, 5 - 00185 Roma

Phosphatidylcholine is the main lecithin phospholipid. Its assumption is mainly due to supplements, to the intravenous treatments of hypercholesterolemia and beauty treatments since it appears to modify the metabolism of cholesterol and triglycerides. Though it is widely used in food industry for the emulsifying properties, an excessive accumulation could cause some effects related to the possible psychostimulant action for the activation of dopaminergic neurotransmitters.
Conventional methods for phosphatidylcholine determination are based on the phosphor present in phospholipid analysis, chromatographic (TLC and HPLC) or spectrophotometric UV-Vis procedures while the interest for faster and cheaper methods is growing.
Enzymatic approaches make the analysis simpler and allow to improve the method precision since they are highly specific and don't include extraction steps. Some procedures can be adopted in phosphatidylcholine determination using free enzymes such as phospholipase A1, A2, C and D.
One of the main drawbacks of using free enzymes is their low stability and high costs. The immobilization of enzymes can increase their operational stability and durability and, at the same time, the reuse lowers costs and time of analysis. Furthermore, these kind of biocatalysts can be coupled with different detector systems.
Among few works reported on immobilized enzymes, phospholipase D coupled with choline oxidase are frequently adopted even if they show a short enzyme life time and a low analytical sensitivity [1,2].
In order to improve these parameters, the aim of this work is to develop a simple, cheap, reproducible and accurate method for phosphatidylcholine determination using immobilized enzymes. Therefore, phospholipase C, alkaline phosphatase and choline oxidase were co-immobilized on the same support in order to increase the reaction rate.
The controlled porosity glass support of pentadecyl-amine type (LCA-CPG), previously packed in a column, has been activated with glutaraldehyde to allow the enzymes to bind covalently.
The synthesized bioreactor has been used, in a flow system, for the determination of phosphatidylcholine in food supplements.
Phosphatidylcholine analysis was followed by spectrophotometric detection of the final product hydrogen peroxide. The system optimization was realized through the study of some parameters such as co-immobilized enzyme concentrations, analyte-bioreactor contact time and flow rate.

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ANODIC STRIPPING VOLTAMMETRY USING GOLD ELECTRODES AS AN ALTERNATIVE METHOD FOR THE ROUTINE DETERMINATION OF MERCURY IN FISH

A. Giacomino[1], A. Ruo Redda[2], M. Malandrino[2], S. Berto[2], S. Squadrone[3], C. Abete[3], M. Rizzi[3], E. Conca[2], O. Abollino[2]
[1]Dipartimento di Scienze e Tecnologia del Farmaco, Università di Torino, Via P. Giuria 9, 10125 Torino
[2]Dipartimento di Chimica, Università di Torino, Via P. Giuria 7, 10125 Torino
[3]Istituto Zooprofilattico Sperimentale del Piemonte, Liguria e Valle d'Aosta (IZSPLV), 10100 Torino, Italy.

The applicability of square wave anodic stripping voltammetry (SW-ASV) conducted with gold electrodes for the determination of inorganic mercury in canned tuna fish has been investigated. Two types of electrodes were tested, namely a solid gold electrode (SGE) and a home-made nanoparticles-modified glassy carbon electrode (AuNPs-GCE). The performance of the two SW-ASV approaches were compared with one another as well as with two spectroscopic techniques, namely conventional cold vapour atomic absorption spectroscopy (CV-AAS) and a direct mercury analyser (DMA-80).
Tuna Fish BCR 463 ([Hg] = 2.85 ± 0.16 mg/kg) and *Tuna Fish ISPRA T22* ([Hg] = 4.43 ± 0.34 mg/kg) were previously analysed to evaluate the efficiency and the accuracy of each technique for mercury quantification in this type of matrix. Then ten samples of canned tunas were purchased in local supermarkets and analysed with the considered techniques.
The results pointed out that both SW-ASV approaches can be considered a suitable alternative to monitor the Hg concentration in tunas, thanks to their consistency with the Hg concentration obtained with spectroscopy. In particular, the higher sensitivity displayed with AuNPs-GCE allowed to reach accurate Hg quantification at concentration values lower than 0.1 mg/kg (fresh weight) with LOQ comparable to that of DMA.

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FAST DETERMINATION OF RESVERATROL IN RED WINE BY PAPER SPRAY TANDEM MASS SPECTROMETRY AND ISOTOPE DILUTION

F. Mazzotti, A. Napoli, D. Taverna, L. Di Donna, G. Sindona
Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci Cubo 12/C, I-87036 Arcavacata di Rende (CS)-Italy

Resveratrol is a phenolic compound, naturally produced by several plants like grapes, berries fruits etc. It is produced in grapes as a defense against toxins, and it is contained within the skins. Paper spray is a mass spectrometry ionization technique that allows for quantitative and qualitative analysis from complex samples reducing prior sample purification steps and without the commonly used chromatography step. The mass spectrometric method was developed using negative polarity according to our experience on the ionization of this molecule;[1] the resveratrol MS/MS spectrum, in negative ion mode, is characterized by few diagnostic fragments. In particular, the ion at *m/z* 185 (*m/z* 191 for labelled internal standard) represents the base peak of the spectrum: this ion is formed for a loss of a ketene molecule by the deprotonated species $[M-H]^-$.[1] This evidence suggests that the ring containing the labelled carbon atom is not involved in the formation of the species at *m/z* 185. The analysis has been performed in MS/MS mode; thus, the quantitative assay has been achieved under MRM conditions monitoring the transition *m/z* 227 → *m/z* 185 for resveratrol and *m/z* 233 → *m/z* 191 for the labelled internal standard. The PS-MS experiment is very fast, the acquisition time is 2 min; the sample obtained after the purification trough C_{18} is loaded directly onto the paper triangle and the analyte is desorbed with methanol 15 μL every 20 sec during the total run time. The purification step with C_{18} cartridge was necessary to prevent the ionization suppression phenomena. The accuracy of the method was determined from spiked samples prepared by adding known quantities of the resveratrol to blank matrix; in the two examined cases the accuracy was higher than 95%. The calculated analytical parameters confirmed the goodness of the proposed approach. The values of LOD and LOQ ranged from 0.5 to 0.8 μg/mL, suggesting that the proposed technique is suitable for a rapid screening of resveratrol in different wine. Finally, to further demonstrate the applicability of the presented PS-MS approach, the same wines were analysed by a classical LC-MS method, as described in literature.[1]

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DETERMINATION OF TRACE ELEMENTS AND FLAVOR CONSTITUENTS IN DIFFERENT TYPES OF FLOUR AND PASTA SAMPLES BY ICP-MS AND HS-SPME-GC-MS

R. Costa[1], A. Albergamo[2], G.D. Bua[2], G. Dugo[2]
[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università degli Studi di Messina, Via Stagno d'Alcontres, 31 – 98166 Messina
[2]Dipartimento di Scienze Biomediche, Odontoiatriche, e delle Immagini Morfologiche e Funzionali, Università degli Studi di Messina, Polo Universitario Annunziata – 98168 Messina
[3]Science4Life S.r.l. a Spin-off of the University of Messina, V.le F. Stagno d'Alcontres 31, 98166 - Messina, Italy

Microwave-assisted sample digestion and inductively coupled plasma-mass spectrometry (ICP-MS) were exploited for the determination of heavy metals (Cd, Hg, Sb, Pb), major (Ca, K, Na) and trace (Fe, Cu, Se, Co, As, Cr, Ni, V) elements, in different types of flour and correlated pasta samples. Obtained data evidenced the effect of technological processing on the content of certain major and trace elements during pasta-making. Indeed, major elements, and some trace nutrients resulted consistently reduced in pasta samples. Nevertheless, levels of heavy metals taken into account by the European Regulation No.1881/2006, resulted to be well within the safety limits, not representing a threat to consumer health.
Furthermore, the flavor profiles of flour and pasta samples were investigated by means of headspace-solid-phase microextraction (HS-SPME), as extraction technique, coupled with multidimensional gas chromatography-mass spectrometry (MDGC-MS), for elucidation of the volatile constituents released by food matrices. Numerous volatiles were determined, belonging to different chemical groups, such as aldehydes, aromatics, furans, ketones, terpenoids. Some constituents are suggested as possible markers for food traceability.

USE OF REVERSED PHASE×REVERSED PHASE LIQUID CHROMATOGRAPHY FOR ANALYSIS OF COMPLEX FOOD SAMPLES

F. Cacciola[1], P. Donato[1], F. Rigano[2], M. Russo[3], P. Dugo[2,3,4], L. Mondello[2,3,4]
[1]Dipartimento di Scienze Biomediche, Odontoiatriche e delle Immagini Morfologiche e Funzionali, Università degli Studi di Messina, Viale Consolare Valeria - 98165 Messina
[2]Chromaleont S.r.l., Viale Boccetta, 70 - 98122 Messina
[3]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, via Álvaro del Portillo 21, 00128 - Roma
[4]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Polo Annunziata, Viale Annunziata - 98168 Messina

Comprehensive two-dimensional liquid chromatography (LC×LC) is a technique of great analytical impact and employed in different fields during the last two decades. Such an analytical approach is deemed as essential, whenever the complexity of the sample overwhelms the separation capability attained by a single separation system, for achieving rewarding results.
Combination of normal phase (NP) and reversed phase (RP) LC separation systems is one of the most orthogonal approaches in LC×LC, whereas the coupling of two RP phases provides considerably lower peak capacity values due to the partial correlation of the two dimensions.
In this work, the use of different gradients strategies in RP-LC×RP-LC allowed to properly tune orthogonality, thus increasing the LC×LC separation space, despite the use of partially correlated stationary phases. Selectivity correlation plots were investigated using different combinations of columns (cyano, amide, C8 and C18 stationary phases) and mobile phases (methanol, ethanol or acetonitrile as phase B). Depending upon the sample to be analyzed combinations of cyano×C18 for sugarcane and red wine, and amide×C8 for biomasses were successfully employed. From a detection viewpoint, photodiode array (PDA) and mass spectrometry (MS) techniques were successfully employed for structure elucidation, representing an effective third added dimension to the LC×LC system.

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DAIRY PRODUCTS: LIPID EVOLUTION DURING SHELF-LIFE

M. Oteri[1], M. Beccaria[2], G. Purcaro[2], G. Micalizzi[2], I. L. Bonaccorsi[1], F. Cacciola[3], P. Dugo[1,2,4], L. Mondello[1,2,4]
[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università degli Studi di Messina, Viale Annunziata - 98168 Messina
[2]Chromaleont S.r.L., Viale Boccetta, 70 - 98122 Messina
[3]Dipartimento di Scienze Biomediche, Odontoiatriche e delle Immagini Morfologiche e Funzionali, Università degli Studi di Messina, Via Consolare Valeria – 98125 Messina
[4]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, Via Álvaro del Portillo 21, 00128 - Rome, Italy

The lipid profile of best-by-date dairy products was investigated to evaluate their possible re-introduction in the food or feed chain. The attention was devoted to fatty acids and triacylglycerols characterization and their variation during storage of fresh-cheese products before and after their best-by-date. Three kinds of cheese were selected, namely a classic Stracchino, Stracchino with the addition of yogurt, and one with the addition of probiotic. The variation of FAMEs and TAGs profiles were studied in order to evaluate the degree of variation occurring in the lipid fraction during storage and after the best-by-date. The classical Schmid–Bondzynski–Ratzlaff extraction method [1] was scaled-down by ten-fold. The GC chromatographic run was sped up after a careful comparison of the result with a conventional analysis. The entire data set of results was evaluated performing both a three-way principal component analysis and a traditional two-way one. The three kinds of samples were well discriminated while a change of the lipid profile over the best-by-date period was particularly significant only for the Stracchino added with probiotic.

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APPLICATION OF COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY FOR ANALYSIS OF FOOD CAROTENOIDS

D. Mangraviti[1], F. Cacciola[2], D. Giuffrida[2] , M. Utczas[3], P. Donato[2], P. Dugo[1,3,4], L. Mondello[1,3,4]
[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Viale Annunziata, 98168 - Messina
[2]Dipartimento di Scienze Biomediche, Odontoiatriche e delle Immagini Morfologiche e Funzionali, Università degli Studi di Messina, via Consolare Valeria, 98125 - Messina
[3]Chromaleont S.r.L., Viale Boccetta, 70, 98100 - Messina
[4]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, Via Alvaro del Portillo 21, 00128 - Rome, Italy

Bioactive molecules are naturally occurring in plants and animal products, with a variety of physiological functions for promoting general body development and disease prevention. Food fractions with identified bioactives with proven health benefits can be incorporated into nutraceuticals and supplements. Carotenoids are an important kind of natural pigment that can be widely found in plants and plant-derived food and products with well-known health-promoting properties . High-performance liquid chromatography (HPLC) represents the method of choice for carotenoid analysis; in particular reversed-phase LC (RP-LC) with both C18 and C30 stationary phases has been extensively employed to achieve the separation of molecules differing in hydrophobicity within a given structural class. On the other hand, normal-phase LC (NP-LC) on silica-based columns is largely employed for carotenoid class separation, according to different polarity (with retention increasing from hydrocarbons to xanthophylls). However, single conventional separation methods sometimes do not provide sufficient resolving power for the separation of target components in many complex samples. Comprehensive two-dimensional liquid chromatography (LC×LC) may be the technique of choice involving two independent LC separation processes with orthogonal selectivities. In this presentation, the application such a technique for the characterization of carotenoids in food products will be shown.

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EVALUATION OF OBETICHOLIC ACID PHARMACOKINETICS AND METABOLISM IN DECOMPENSATED LIVER CIRRHOSIS BY LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY.

A. Roda[1], R. Aldini[2], S. Spinozzi[1], P. Franco[1], M. Cont[3], L. Adorini[4]
[1]Department of Chemistry "G. Ciamician", University of Bologna, Bologna, Italy
[2]Department of Pharmacy and Biotechnology, University of Bologna, Bologna, Italy
[3]INBB, Istituto Nazionale Biostrutture e Biosistemi, Roma, Viale delle Medaglie d'Oro, 305, 00136, Roma, Italy
[4]Intercept Pharmaceuticals, 450 W 15th Street, Suite 505 | New York, NY 10011, USA

Obeticholic Acid (OCA) is a semisynthetic bile acid (BA) analogue and potent FXR agonist. It is the analogue of chenodeoxycholic acid (CDCA), with an ethyl group in the 6α-position that confers to OCA its potent FXR agonistic activity [1]. OCA is under medical investigation as drug for the treatment of hepatic pathologies, such as Primary Biliary Cirrhosis (PBC) [2] and Nonalcoholic Steatohepatitis (NASH) [3]. Considering its current use in clinical practice, it is important to evaluate OCA pharmacokinetics and metabolism in a model of liver disease to determine potential undesirable localization in specific organs or biological fluids, especially when chronically administered. With this aim an HPLC-ES-MS/MS method was developed [4] to quantify endogenous BA, OCA and its main metabolites in plasma, liver, stools, intestinal contents, urine and kidneys samples. The developed method proved to be accurate (bias%<15%), precise (CV%<12%) and sensitive (LOQ<10 nM); matrix effects doesn't significantly affect the analysis accuracy and determined recoveries are higher than 80%. These features make the method adequate for measuring OCA and endogenous BA in biological fluids/tissues and for obtaining a complete profile of them. The method was successfully applied to a study of OCA pharmacokinetics and metabolism in a rat model of induced decompensated liver cirrhosis by CCl4 inhalation for 13 weeks. In addition, OCA hepatic metabolism and biliary secretion were studied in cirrhotic rats using the bile fistula model after intravenous administration. Results showed that OCA plasma concentrations were not at risk of producing unsafe levels in specific organs or tissues.

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IONOMIC RESPONSES OF WILD AND TRANSGENIC *NICOTIANA LANGSDORFFII* PLANTS EXPOSED TO HEAT STRESS

E. Scalabrin[1], M. Radaelli[1], G. Rizzato[1], G. Capodaglio[1,2]
[1] Dipartimento di Scienze Ambientali, informatica e statistica, Università Ca'Foscari di Venezia, Via Torino, 155 – 30172 Mestre (Ve)
[2] Istituto per la dinamica dei processi ambientali-CNR, Via Torino, 155 – 30172 Mestre (Ve)

Plants are composed of chemical elements, which uptake, distribution and accumulation are controlled by genetic and environmental factors. Particularly, plants face adverse or limiting conditions by activating a complex system of physiological and metabolic responses. High temperatures, together with other stress factors induced by global climate change, may significantly affect the growth and development of plants; heat stress conditions showed to delay plant's growth, damage its cell membranes, increase transpiration and reduce the opening of the stomata. In this work, *Nicotiana langsdorffii* plants, wild and transgenic for the *Agrobacterium rhizogenes* rol C and rol D gene and the rat glucocorticoid receptor (GR) gene, were exposed to heat stress. The responses of the transgenic plants to the abiotic stresses were assessed by the analysis of the plant ionomic profile, the metabolomic data and the phytormonal profile (1,2). Simultaneous determination of 12 elements was carried out by ICP-MS equipped with a collision/reaction cell (ICP-ORS-MS). WT, Rol D and Rol C plants showed higher changes both in the ionomic and in the metabolic profile, suggesting that these genotypes could be more affected by heat stress exposition. On the contrary GR plants showed almost unchanged values of many elements and organic compounds (including phytohormone and lipids) indicating that this genetic modification could provide a higher plant resistance toward heat stress. Statistical analysis permitted to highlight the main significant differences among the metabolic responses of the examined genotypes.

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FOURIER TRANSFORM INFRARED SPECTROSCOPY FOR THE LEATHER QUALITY CONTROL IN THE ECO FRIENDLY TANNING CYCLE

E. Bramanti[1], V. Della Porta[1], M. Onor[1], B. Campanella[1,2], A. D'Ulivo[2], E. Pitzalis[1], M.C. Mascherpa[1], A. Dall'Ara[3]
[1]Istituto di Chimica dei Composti Organometallici - UOS di Pisa, Consiglio Nazionale delle Ricerche (CNR), Via Moruzzi 1 – 56124 Pisa
[2]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13 – 56124 Pisa
[3] Unità Tecnica Tecnologie dei Materiali Faenza (UTTMATF)

The aim of the LIFETAN project[1] is the demonstration of the use of innovative natural products and technologies for the bating, defatting, fatting, dyeing and tanning phases in the whole leather tanning process.
The main environmental, social and economic goal is the replacement of current commercial chemical and toxic products with natural products in the whole tanning cycle, in order to establish a significantly eco-sustainable and convenient business for companies. The project aim is the production of high quality leather products tanned with the new products and compared wilth the traditional one. Six new tanning formulations with natural products will be proposed and tested, characterized by higher biodegrability and performance. FTIR is a valuable useful technique to investigate at molecular level the interaction of new products with the leather proteins. The FT-IR analysis of amide I band gives information both in terms of the absorbance ratios at two different wavelengths (e.g. the 1654/1690 cm^{-1} absorbance ratio to evaluate the collagen cross linking) and the analysis of the single components found by peak fitting (conformational analysis) [2, 3].

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FTIR STUDY OF THE INTERACTION BETWEEN NATURAL DEFATTING AGENTS AND LEATHER PROTEINS FOR THE MONITORING OF THEIR ENVIRONMENTAL IMPACT

V. Della Porta[1], M. Corsi[2], R. Bianchini[2], M. Onor[1], E. Pitzalis[1], A. D'Ulivo[1], E. Bramanti[1]
[1]Istituto di Chimica dei Composti Organometallici - UOS di Pisa, Consiglio Nazionale delle Ricerche (CNR), Via Moruzzi 1 – 56124 Pisa
[2]Dipartimento di Chimica 'Ugo Schiff', Università di Firenze, Sesto Fiorentino

Our work aimed to demonstrate the effective capability of natural leather defatting agents to replace the commercial products and reduce the environmental impact of defatting effluents.
Leather manufacturing combines indeed several working phases that transform waste materials of the cattle industry such as animal skins into valuable products such as the leather goods. The leather defatting is an important preparatory step prior to tanning to remove fat properly. A good balance of defatting is required, to allow the stabilization of the skin into leather by the tanning agents, whilst keeping the softness and smoothness of the original animal skin.
Chlorinated paraffins and alkyl phenol derivatives are common defatting agents employed in the leather industry but in the last decades they have been replaced by ethoxylated long chain because of their environmental impact and hazards to human health. Nevertheless, the biodegradability of ethoxylated alcohols is critical, because branched ethoxylated alcohols tend to accumulate overtime and linear compounds may be degraded slowly. Furthermore, degreasing agents contain also ethoxylated derivatives of vegetable oils and sugars. This complex mixture of chemicals is quite difficult to manage downstream, when effluents are discharged.
To simplifying the complexity of the commercial products and reduce the environmental impact of defatting effluents, new defatting agents based on the processing of the naturally occurring lactose, a waste substance of the dairy industry produced in hundreds of thousands of tonnes per year, were developed.
In this work we studied the interactions natural defatting agents/leather protein by Attenuated Total Reflectance- Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Thermogravimetric Analysis (TGA).
The monitoring of the environmental impact of defatting effluents from the use of new formulations was carried out through metal analysis.

METHOXYPHENOLS IN ARCTIC SEAWATER

S. Padoan [1], E. Barbaro [1,2], R. Zangrando[2], O. Karroca[1], C. Barbante[2], A. Gambaro[1,2]

[1] Department of Environmental Sciences, Informatics and Statistics, University of Venice, Ca' Foscari, Via Torino 155, 30170 Venezia, Mestre, Italy

[2] Institute for the Dynamics of Environmental Processes CNR, Via Torino 155, 30170 Venezia, Mestre, Italy

Methoxyphenols are organic and semi-volatile compounds that are used as specific biomarkers of combustion events. These compounds are able to provide information about the type of combusted biomass [1]. Recently, several studies [2] have highlighted that the presence of methoxyphenols in polar areas are attributable not only to biomass burning but also to local marine sources.

The purpose of the present work was to determine free phenolic compounds in both dissolved and particulate fractions in Arctic seawater samples. We analyzed 67 samples of coastal seawater collected near the coast line of Kongsfjord during the Arctic sampling campaign 2015.

The quantitative determination has been performed using a HPLC-MS/MS method developed by Zangrando et al. [3]. Vanillic acid, vanillin, p-coumaric acid, syringic acid, isovanillic acid, homovanillic acid, syringaldehyde, acetosyringone and acetovanillone were determined. In dissolved phase there was a higher concentration of methoxyphenols than in the particulate fraction. The most abundant compounds in our samples were vanillic acid, vanillin, acetovanillone and p-coumaric acid.

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LEVELS OF VOLATILE ORGANIC COUMPONDS IN AMBIENT AIR OF ROME

P. Avino[1], M. Manigrasso[1] and M.V. Russo[2]
[1]DIT, INAIL Settore Ricerca, via Roberto Ferruzzi, 38/40 - 00143 Roma
[2]Dipartimento Agricoltura, Ambiente e Alimenti, Università degli Studi del Molise, via De Sanctis - 86100 Campobasso

Hydrocarbons are a significant component in urban air because of combustion, solvent and fuel evaporation and tank leakage; most of aromatic compounds are considered as toxic air contaminants (e.g. benzene) or potential toxic air contaminants (e.g. toluene, xylenes).
Further, the NMHCs play a key role in the formation of photochemical air pollution. They are considered as precursors for ozone production at the ground level when the sunlight and nitrogen oxides are present. NMHCs and aromatic hydrocarbons participate in the formation of urban and suburban photochemical smog with their concentrations influencing greatly the total ozone in different percentage [1]. Derwent et al. [2] were the first to determine that m-xylene, trimethylbenzenes and C_3-C_4 alkenes produce more ozone than ethylene.
In this paper, we report the results obtained during an intensive measurement campaign in wintertime. The air quality analysis was conducted by two different ways. About 50 air samples were taken by canisters in 4 different locations in Rome during 3 days to investigate the non-methane and aromatic hydrocarbon composition; at the same time, automatic analyzers and Differential Optical Absorption Spectrometry (D.O.A.S.) investigated traditional atmospheric pollutants like ozone, nitrogen dioxide, nitrous acid, carbon monoxide, formaldehyde, benzene and toluene in downtown Rome. Finally, we calculated the percentage contribution of each determined VOC to ozone formation in the ambient air of Rome, comparing these values with other studies reported in literature.
The results obtained show that the m-xylene, the toluene and 1,2,4-trimetilbenzene are the compounds that compete in better percentage to the formation of ozone in Rome. Further, in the same period the trends of benzene, toluene, CO, NO and PAH are decreased, expecially because of introduction of both the green fuel and the autovehicular catalytic pot. But, even if the pollutant levels are decreasing, the sources are still the same and, in particular, the emission from the incomplete combustion of LPG is the most important source of pollution in Rome.

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AN ARCHAEOMETRIC STUDY OF IMPERIAL OIL CLAY LAMPS FROM GNATIA (FASANO-BRINDISI, SOUTHERN ITALY)

L.C. Giannossa[1], F. Mastrorocco[2], C.S. Fioriello[3], M. Pallara[4], R. Laviano[4,§], A. Mangone[2,§]
[1]Dipartimento di Economia, Management e Diritto dell'Impresa, Università degli Studi di Bari Aldo Moro, Largo Abbazia Santa Scolastica, 53 - 70124 Bari
[2]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via Orabona 4 – 70126 Bari
[3]Dipartimento di Studi Umanistici, Università degli Studi di Bari Aldo Moro, Piazza Umberto I-1 – 70121 Bari
[4]Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari Aldo Moro, Via Orabona 4 – 70126 Bari
[§] Centro Interdipartimentale "Laboratorio di Ricerca per la Diagnostica dei Beni Culturali", via Orabona 4 - 70126 Bari

This study is part of a wider project on the oil clay lamps coming from Apulia, aimed at acquire information on the complex phenomenon of imports-exports-imitations of this class of objects.
The documentation collected on the clay lamps from the Roman age in Apulia allows drawing a preliminary picture of both the local production and the diffusion and circulation of these materials between the I cent. BC and the beginning of the IV cent. AD.
In Apulian contexts, the richness and heterogeneity of the available information do not allow a clear definition of the commercialization and diffusion yet, but thanks also to the use of diagnostic archaeometry applied to these lychnological focused contexts, it is possible to establish the tendencies and orientations which are useful to the definition of a socio-economic panorama of the territory.
We have analyzed 48 Imperial Age oil lamps (end I-III cent. AD), 46 found in the archaeological excavations of Gnatia and 2 in the Roman 'west necropolis' discovered in Brindisi. Stylistically, the artworks show rounded and short beaks and 'beads' motifs.
We have determined chemical elements in ceramic bodies by ICP-MS and treated the compositional data by multivariate statistical treatment (PCA). We have performed mineralogical and petrographic characterization of ceramic bodies and coatings by OM and SEM-EDS.
Comparison of the results obtained with those both on Late Antiquity lamps found in Gnatia (end IV- end VI cent. BC) and on 'broad line ware' certainly produced in Gnatia (end VI cent. AD), makes it fascinating and possible to attribute to egnatine production centers, or however to that regional area, some oil clay lamps that the traditional autoptical-chronological analysis ascribed to Northern African or Center Italian areas.

PLATINUM AND RHODIUM IN WINES

S. Orecchio[1], D. Amorello[1], S. Barreca[2], E. Gulli
Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche. Università di Palermo, Viale delle Scienze, I-90128, Palermo, Italy. E-mail: santino.orecchio@unipa.it
[2]ARPA, Lombardia, Milano

For the first time, the concentrations of Pt and Rh in 42 different alcoholic beverages (white and red wines, vodka and brandy) produced in Italy, Malta and Gozo were investigated. Only the voltammetric techniques, in particular, differential Pulse Voltammetry (DPV/a) and Adsorptive Stripping Voltammetry (AdSV) were used for the determination of Pt and Rh respectively.
Accuracy was tested with standard addition method and recoveries ranged from 90% to 98%.
In analyzed wine samples, Pt and Rh concentrations are in the ranges from 3 to 470 μg L-1 and from 0.0006 to 0.36 μg L-1 respectively. We found a Pt/Rh ratios ranged from 37 to 180000, in quite disagreement with the ratio in catalytic converters. Unlike other investigated matrices (settled dust matter), the concentrations of Pt and Rh are not correlated, suggesting that the grape or the plant (vitis vinifera) treated the two metals very differently.
Daily intakes (DIM) of Pt and Rh were calculated. Consuming 200 mL/day of wine, this supply from 0.6 to 94 μg and from 0.00012 to 0.072 μg of platinum and rhodium for person respectively.

A GLOBAL SIGNATURE OF THE ANTHROPOGENIC IMPACT ON THE CLIMATE SYSTEM FROM TALOS DOME ICE CORES (ANTARCTICA)

Battistel D.[1,2], Kehrwald N.M.[3], Zennaro P.[2], Barbante C.[1,2]
[1]Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Cà Foscari Venezia, Via Torino, 155 – 30702 Mestre Venezia
[2]Institute for the Dynamics of Environmental Processes, IDPA-CNR, Via Torino, 155 – 30702 Mestre Venezia
[3]U.S. Geological Survey, Geosciences and Environmental Change Science Center, Lakewood, CO 80225, USA

Antarctic ice cores can provide biomass burning records in regions where paleofire data are limited. Levoglucosan (1,6-anhydro-β-D-glucopyranose), a specific molecular marker for biomass burning, was determined in Talos Dome ice (TALDICE) core to reconstruct mid-late Holocene fire history, using an analytical method based on HPLC/MS/MS. The record shows a gradual increase in fire activity from ~5000 yr BP and intense fire events (mega-fire) 2000-2500 yr BP. The occurrence of mega-fire events was already observed in previous studies carried out in NEEM (Greenland), approximately in the same time period [1]. The increase in fire activity in NEEM was ascribed to anthropogenic factors rather than natural, since it cannot be explained only considering boreal climate parameters. Models (JSBACH, KK10 and HYDE) demonstrate that deforestation for agriculture in Europe and Asia resulted in major biomass burning during this period. Unlike NEEM, which is surrounded by large landmasses, Talos Dome ice core is located far away from any biomass burning source and, during the Holocene, the major source for atmospheric transport in East Antarctica was from Australia and South America. Levoglucosan record doesn't correlate with crustal elements and dust in Talos Dome and it is consistent with the Global Charcoal Database records from Australasia and South America. However, in Southern Hemisphere charcoal dataset is under-represented. Talos Dome levoglucosan record has been interpreted as a hemispherical signal that cannot be explained only considering natural climate forcing, since solar radiation increases up to 2000 years BP and the mean global temperature slightly decrease up to pre-industrial period, in contrast with our observations, and the anthropogenic factor have to be invoked for explaining this trend.

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RECONSTRUCTION OF THE MAYA-DRIVEN EARLY ANTHROPOCENE IN CENTRAL GUATEMALA FROM MULTIELEMENTAL PROXIES IN A LAKE SEDIMENT RECORD

A. Marchetti[1], M. Roman[1,2], T. Kirkgeorg[1], W.R.L. Cairns[2], M. Radaelli[1] and D. Battistel[1]

[1] Ca' Foscari University of Venice, Department of Environmental Sciences, Statistics and Informatics (DAIS), Via Torino 155, 30172 Venice Mestre, Italy; [2] Institute for the Dynamics of Environmental Processes (IDPA-CNR), Via Torino 155, 30172 Venice Mestre, Italy

The Maya population is recognized as one of the first whose activities have significantly impacted the natural environment much earlier than industrial revolution [1]. Still, the actual scale of such impacts and their possible role in driving the collapse of Maya civilization are currently a matter of debate [2]. In this study, a sedimentary record from Lake Petén Itzá, central Guatemala, was analysed for trace, platinum group and rare earth elements to reconstruct the evolution of their concentration, enrichment factor and flux over the last 6000 years. Complementary measurements of total organic and inorganic carbon provided contextual data on the variation of sediment's composition over time.

The results showed substantial alterations of the natural geochemical equilibrium due to the deforestation, agricultural practice and general land use during the over 2000 years of Maya occupation, strongly associated to demographic trends and the sequence of cultural periods. Increased soil erosion, exacerbated by high rainfall, raised the flux of traces-depleted clastic materials to the Lake from Maya settlement around 1000 B.C., up to a maximum between 400 B.C. and 200 A.D. During the subsequent classical period, at the top of demographic expansion, drier climate and the introduction of more sustainable agricultural practices mitigate the erosion processes, but a substantial recovery of the ecosystem took place only after the sudden collapse of Maya civilization around 1000 A.D., and the consequent restoration of tropical forest. While possible signs of volcanic events were observed, which could have affected some human activities (e.g. production of ceramics), no significant evidences of pollution liked to metallurgy was revealed during Maya occupation.

The results are discussed in the context of literature data including paleofire and paleovegetation reconstructions, and archaeological proofs, to provide a comprehensive view of the state-of-the art in the knowledge of how the Maya civilization transformed the surrounding environment.

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ESEM-EDS ANALYSIS OF METAL SUBMICRO- AND NANOPARTICLES AS EMERGING CONTAMINANTS IN AIR, RAW MATERIALS AND FOOD PRODUCTS

M. Mattarozzi[1], F. Bianchi[1], D. Catellani[2], M. Suman[2], M. Careri[1]
[1]Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze, 17/A – 43124 Parma
[2]Barilla G.R. F.lli SpA, Advanced Laboratory Research, Via Mantova, 166 – 43122 Parma

Nanoparticles (NPs) can occur naturally, or can be produced unintentionally from human activities or be intentionally engineered, thus making human exposure almost inevitable. NPs can contaminate food products through the migration of nanostructured additives from food packaging as well as from environmental contamination. In this context, there is an urgent need to develop adequate analytical methodologies for detecting and characterizing NPs in complex matrices as finished food products [1]. Electron Microscopy equipped with Energy-Dispersive X-ray Spectroscopy (EDS) permits to visualize NPs, thus determining their shape, size and aggregate state, and to assess their elemental composition. Based on our experience [1], in the present study, Environmental Scanning Electron Microscopy (ESEM)-EDS was used for qualitative and quantitative analysis of metal submicro and nanoparticles in air, raw materials and food products along pasta production chain (wheat ear, wheat, semolina and pasta). Signal arising from backscattered electrons was recorded for Z-contrast, working in low vacuum conditions (70 Pa). Particle counting and identification were performed on automatically acquired images over a proper representative filter area. In the case of raw materials and food products the particles were collected on polycarbonate 0.1 μm filters after immersion in milli-Q water. As for airborne particles, size-fractionated sampling was performed by an eight-stage cascade impactor (final stage: 0.1 μm) exposed for 72 h. In the filters from wheat ear, wheat, semolina and pasta samples, particles (< 800 nm) containing mainly Fe and Ti were identified, most of them having dimensions < 150 nm, whereas in air filters the elements mainly identified were Fe, Mn and Pb.

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CHEMICAL CHARACTERIZATION OF ANCIENT LITURGICAL VESTMENT (CHASUBLE) BY ICP-OES

D. Amorello[1], S. Barreca[2], M. Bruno[1], A. Milia, S.Orecchio[1], A. Pettignano[3]
[1]Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche. Università di Palermo, Viale delle Scienze, I-90128, Palermo, Italy. E-mail: santino.orecchio@unipa.it
[2]ARPA, Lombardia, Milano
[3] Dipartimento di Fisica e Chimica, Università di Palermo. Viale delle Scienze, I-90128, Palermo, Italy

This paper presents the chemical characterization of the yarns of an ancient liturgical vestment (chasuble). The samples have been analyzed for Al, Ag, Au, Cd, Co, Cr, Cu, Ni, Pb and Zn using amounts always less than 1 milligram by Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES). Except a sample, silver is the most abundant element in all the yarns. In the samples containing silver, it ranged from 68 to 97%. Only two samples contain aluminum. Although the investigated chasuble is recorded in the inventory as an artifact of the XV century, a part of the yarns is composed of materials attributed to later period. In fact, the voluntary use of aluminum in metal alloys is due to later periods. A yarn appears silver and apparently could be considered equal to others but does not contain silver. The metallic effect is achieved by using a cheaper metal (lead).

N-[DI(PYRIDIN-2-YL)METHYL]ALLYLAMINE AS NOVEL COPPER-COMPLEXING FUNCTIONAL MONOMER FOR ION IMPRINTING

C. Giovannoli, M. Malandrino, G. Spano, G. Volpi, L. Anfossi, C. Baggiani
Dipartimento di Chimica, Università degli Studi di Torino, Via Giuria, 5 - 10125 Torino

Ion imprinting technology has been increasingly developed during the last years on the principle of molecular imprinting to provide versatile receptors able to efficiently recognize inorganic ions. The selective recognition of ions, their extraction and quantification from aqueous media is one of the main goals in a large range of applications in analytical field.
The general procedure for the preparation of ion imprinted polymers (IIPs) consists in the formation of a stable ligand-metal complex and its co-polymerization with a cross-linker in order to create three-dimensional recognition cavities inside the polymer network. Similarly to MIPs, at the end of the synthesis template ions have to be removed from the binding sites to make the polymer usable. Owing to particular coordination and/or electrostatic interactions, IIPs are generally compatible with aqueous media making easier their application in such media with respect to MIPs. However, a successful application of IIPs strongly depends on various factors including a sounding choice of the complexing agent and of all the polymerization components.
In this work we present N-[di(pyridin-2-yl)methyl]allylamine as a novel functional monomer with complexing properties towards Cu(II) ions. The corresponding IIP was prepared in methanol by thermopolymerization in the presence of the pre-formed complex between Cu(II) and the complexing monomer in a 1:2 metal-to-ligand ratio, 2-hydroxyethylmethacrylate as secondary monomer, ethylenedimethacrylate as cross-linking agent and AIBN as radical initiator.
After the exhaustive removal of the template ion with EDTA, the binding properties of the imprinted and non-imprinted polymers were studied by partition experiments where a fixed amount was equilibrated with variable concentration of Cu(II). After the equilibrium was reached, the free amount of Cu(II) was separated from the polymer and measured by ICP-OES. In order to evaluate the selectivity of the polymers the same experiments were achieved by using other metal ions (i.e. Cd, Zn, etc).
It was found that the novel IIP exhibits good binding properties in terms of equilibrium binding constant and binding sites concentration and interesting selectivity towards the chosen target ion.

DETERMINATION OF EMERGING POLLUTANTS IN WATER: THE PASSIVE SAMPLING APPROACH

E. Magi, M. Di Carro, C. Mirasole, B. Benedetti
Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, via Dodecaneso 31 - 16146 Genova

In the last decade, the growing interest in emerging pollutants has stimulated research on new sensitive and selective methods for their determination in different matrices; in particular their occurrence in the aquatic environment is mainly due to the incomplete removal in sewage treatment plants [1]. In spite of the remarkable progress in analytical techniques for trace analysis, their very low levels of concentration in environmental waters, typically in the low ng/L range, require preconcentration procedures such as SPE, SBSE, SPME or passive sampling. The latter approach allows the integrative monitoring of aqueous pollutants, due to the dynamic interaction with high volumes of water, and the detection of contaminants deriving from episodic events, not always possible by spot sampling. POCIS (Polar Organic Chemical Integrative Sampler) are passive samplers designed to sequester and concentrate polar organic chemicals in situ, which enable the determination of their time-weighted average (TWA) concentration in water [2].
In this work, POCIS followed by target liquid chromatography-tandem mass spectrometry was employed for the determination of nonsteroidal anti-inflammatory drugs (NSAIDs) and other emerging pollutants in surface waters. POCIS were deployed for two and four weeks in order to detect the analytes at ultra-trace levels. Quantitative analysis was carried out by mass spectrometry in both positive and negative ionization mode and multiple reaction monitoring. For the evaluation of the TWA concentration the sampling rates R_s, specific for each compound, were calculated by means of a simple calibration system developed in our laboratories [3-4].

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LEAD(II) AND CADMIUM(II) REMOVAL FROM AQUEOUS SOLUTIONS USING HAZELNUT AND ALMOND SHELLS SORBENT MATERIALS

S. Cataldo, A. Gianguzza, N. Muratore and A. Pettignano
Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze, Edificio 17 - 90128 Palermo, Italy.

Removal of toxic metal ions from natural and waste waters is of great importance for the health of living organisms and for environmental protection. Alternatively to the conventional chemical treatments, such as precipitation, reverse osmosis, etc, biosorption shows a growing interest for toxic metal ions removal from contaminated aqueous solutions.
The sorption ability of every type of biomass towards metal ions depends on many variables that characterize the solution. Among these, the ionic strength (I) is one of the most important and cannot be neglected during an accurate adsorption study.
For this reason and with the aim of quantitatively define the influence of I, here are reported the results of kinetic and thermodynamic studies on the sorption capacity of Hazelnut (HS) and Almond (AS) shells toward Pb(II) and Cd(II) in NaCl aqueous solution in a wide I range ($0.05 < I$ (mol L^{-1}) < 0.5) at room temperature. The formation of chloride complexes have been always considered. To avoid the hydrolysis of the metal ions the pH value of solutions was kept at 5. HS and AS have been grinded, washed and sieved before using. The materials were characterized by FT-IR and SEM-EDX analysis. The FT-IR spectra showed the presence of numerous O-donor sites indicating that sorption process occurs by chemical interaction of metal ions with these binding groups.
The residual metal concentration in aqueous solutions during the kinetic and equilibrium experiments was measured by Differential Pulse Anodic Stripping Voltammetry (DP-ASV).
Several kinetic and isotherm equations were used to fit the experimental data. The pseudo second order equation was the best in terms of fit for all the systems investigated. Although all the isotherm models fitted properly the equilibrium data, the Langmuir model was the best one for the Pb(II)-HS/AS systems, whereas Sips model showed the best results for the Cd(II)-HS/AS systems.

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MULTIPLE SCLEROSIS AND ENVIRONMENTAL FACTORS

J.I. Lachowicz[1], P. Valera[1], A. Sanna[1], V.M. Nurchi[1], G. Crisponi[1], L. Lorefice[2], E. Cocco[2]
[1]University of Cagliari, Department, Department of Civil-Environmental Engineering and Architecture, via Marengo 2, 09123 Cagliari, Italy, lachowicz@unica.it
[2]University of Cagliari, Multiple Sclerosis Center, Department of Public Health, Clinical and Molecular Medicine, via Is Guadazzonis, 2, Cagliari, Italy

MS prevalence presents a decreasing gradient in Europe from the Nordic countries to the Mediterranean ones[1]; an exception is Sardinia, which represents a high-risk area in spite of its geographical location[2]. However, a rise in the MS incidence has been seen almost worldwide in the last decades[3]. In particular, it was recently shown that Southwest Sardinia (SWS) is a high-risk area for MS with a prevalence of 210.4/100,000[4]. Among different environmental factors potentially involved to the disease occurrence[5], some elements and compounds are considered in this study. In particular, we are exploring the contribution by heavy metals and some others elements naturally occurring in the environment, but in different values, depending on the lithology. Among such elements are Ba, Cd, Cu, Hg, Pb, Zn.
Here we present geochemical sketch maps of South Western Sardinia obtained by processing of analytical data related to different matrices (stream sediments and waters). Morever, we present some preliminary ICP-MS and ICP-AES determinations of the heavy metals and trace elements values (eg, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Si, Th, U, Zn) in blood samples from first healthy control (HC) sampling.

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SIMULTANEOUS VOLTAMMETRIC DETERMINATION OF TRAFFIC-RELATED AND POTENTIALLY TOXIC METALS IN MARINE ORGANISMS TO EMPLOY AS POSSIBLE POLLUTION BIO-MONITORS

D. Melucci[1], F. De Laurentiis[1], A. Zappi[1], M. Locatelli[2] and C. Locatelli[1]
[1]University of Bologna, Department of Chemistry «G. Ciamician», Via F. Selmi 2, I-40126 Bologna (Italy)
[2]University "G. d'Annunzio" Chieti-Pescara, Department of Pharmacy, 66100, Chieti-Italy;

The present paper reports a new electroanalytical procedure for the simultaneous voltammetric determination of ultra-trace platinum(II), palladium(II), rhodium(III), copper(II), lead(II), Cadmium(II) and Zinc(II) by square wave adsorptive catalytic stripping voltammetry (SWAdCSV) in mussels and clams, possible bio-monitors, using a conventional three-electrodes voltammetric cell: a stationary hanging mercury drop electrode (HMDE) as working electrode and a platinum electrode and an $Ag|AgCl|KCl_{sat}$ electrode as auxiliary and reference electrodes, respectively 0.1 mol L^{-1} HCl + $2.3x10^{-4}$ mol L^{-1} dimethylglyoxime (DMG) + formazone complex [0.7 mmol L^{-1} formaldehyde + 1.5 mmol L^{-1} hydrazine in 0.1 mol L^{-1} HCl] + 8.5 $x10^{-2}$ mol L^{-1} $NaBrO_3$ + $4.9x10^{-4}$ mol L^{-1} EDTA-Na_2 was employed as the supporting electrolyte

The analytical procedure was verified by the analysis of the standard reference materials Mussel Tissue BCR-CRM 278 and Oyster Tissue NIST-SRM 1566a. Precision and accuracy, expressed as relative standard deviation and relative error, respectively, were generally lower than 7 % in all cases.
Once set up on the standard reference materials, the analytical procedure was transferred and applied to mussels and clams sampled in the Po river mouth area.
A critical comparison with spectroscopic measurements is also discussed.

MOBILITY AND AVAILABILITY OF METALS IN MARINE SEDIMENT CORES COLLECTED IN ROSS SEA, ANTARCTICA

M. Malandrino[1], A. Giacomino[2], S. Buoso[1], C. La Gioia[1], F. Burgay[1], E. Conca[1], O. Abollino[1]
[1]Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria, 5 – 10125 Torino
[2]Dipartimento di Scienze e Tecnologia del Farmaco, Università degli Studi di Torino, Via Pietro Giuria, 9 – 10125 Torino

Marine sediments are sinks and repositories of matter recirculated in the environment by a number of different processes. They behave as environmental archives, providing a key to the understanding of the processes occurring in a given region in the course of time.
During the XX Italian Antarctic Survey, several sea sediment cores were sampled in the Ross Sea, Antarctica. In this study, we characterized the inorganic composition of four sediment cores collected in different localities of Terra Nova Bay (TNB) in the Ross Sea, an area of major environmental interest as it hosts a number of crucial processes connecting atmospheric transport with the Southern Ocean system [1]. The total concentrations of major, minor, and trace elements were determined. The results were treated with chemometric techniques. The elemental composition of the cores was found to be mainly dominated by terrigenous elements, but it is also influenced by biological factors, such as, for example, the presence of corals in one of the core (coded as H2) [2].
Since the knowledge of the total concentration of elements is not sufficient to understand their reactivity and, in general, their behavior in the environment, we applied the modified Bureau of Community Reference (BCR) three-step sequential extraction procedure. With this procedure, we evaluated the concentration, the distribution and the bioavailability of eight metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn).
Finally, we investigated the geological and biological components of the sediment through a XRD and SEM analyses respectively.
The knowledge of the metal distribution across these Antarctic sediment cores allowed us to assess long-term climatic changes and possible natural background values in this specific environment. Furthermore, the results showed a separation between higher and lower sections of the core that suggests a stronger fingerprint from biogenic and geological processes, respectively.

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A NEW EXPERIMENTAL SCHEME FOR THE DEFINITION OF THE NATURAL FORMATION PATHWAYS OF PBDEs

S. Giuliani[1], L.G. Bellucci[1], S. Pizzini[2], M. Vecchiato[3], R. Piazza[3,2]
[1]Institute of Marine Sciences, National Research Council (CNR-ISMAR), Via Gobetti, 101 - 40129 Bologna, Italy
[2]Institute for the Dynamics of Environmental Processes, National Research Council (CNR-IDPA), Via Torino, 155 - 30172 Venice, Italy
[3]Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Via Torino, 155 - 30172 Venice, Italy

Our research group has recently investigated POP contamination in the Nador Lagoon (N-E Morocco). Such studies have highlighted a peculiar situation: measurable total concentrations of Polychlorinated biphenyls (PCBs) and Polybrominated diphenyls ethers (PBDEs) were found at depths corresponding to times when these chemicals were not yet artificially produced [1,2]. Post-depositional reworking processes were suggested in order to explain the presence of PCBs shortly before the 1930s [1], but the case of PBDEs was considerably more puzzling: the latter compounds were detected at depths corresponding to the early 1950s at the maximum value measured in the entire sedimentary record [2]. Physical mixing and/or bioturbation processes might have contributed to setting off vertical movements along the core, but it is unlikely that they alone could have produced the observed concentration peak at depth. An additional unforeseen process might therefore have been at work. Two of the most abundant naturally occurring structural analogues of PBDEs (*i.e.* 6MeO-BDE-47 and 6OH-BDE-47) are very similar to BDE-47 (the most abundant congeners detected in our studied sediments). Therefore, we hypothesized that reducing conditions in buried sediments might have favoured demethylation and dehydroxylation of these compounds to BDE-47. Following bromination processes might then have produced the other observed congeners.
The formation of PBDEs from naturally synthesized polybrominated compounds in sediments is a fascinating hypothesis and, if verified, could pave the way to studies aimed at the definition of sources and origin of PBDEs. In this presentation we propose a rationale for a new experimental procedure aimed at studying this formation pathway and at verifying its presence in reducing sediments at laboratory scale.

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NON-LEGACY CONTAMINATION BY 3,3'-DICHLOROBIPHENYL IN MARINE SPECIES: COMPARISON BETWEEN MEDITERRANEAN AREA AND ANTARCTIC REGION

S. Pizzini[1], C. Sbicego[2], M. Grotti[3], G. Cozzi[1], R. Piazza[2,1]
[1]Institute for the Dynamics of Environmental Processes, National Research Council (CNR-IDPA), Via Torino, 155 - 30172 Venice, Italy
[2]Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Via Torino, 155 - 30172 Venice, Italy
[3]Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso, 31 - 16146 Genoa, Italy

Polychlorinated biphenyls (PCBs) are among the main classes of persistent organic pollutants (POPs) and are largely distributed in every environmental compartment worldwide. The sources of PCB contamination are commonly associated to the industrial use of commercial mixtures, such as Aroclors, which were banned from production in 1979. However, different sources of PCBs, unrelated to the commercial distribution of mixtures, have been recently identified. In particular, the congener 3,3'-dichlorobiphenyl (PCB-11) has been considered as a marker of non-Aroclor PCB contamination in the environment [1,2].
Along with the other lower chlorinated congeners, PCB-11 is significantly affected by long-range atmospheric transport (LRAT) and has been found in almost every environmental matrix worldwide, including Polar regions.
Despite the concern and the evidence about the global distribution of non-legacy PCB contamination, little is known about the potential adverse health effects of PCB-11 and its uptake through the food chain.
The first aim of this work is to investigate and quantify the presence of the PCB-11 congener in samples of bivalves as an indication of non-legacy PCB contamination in biota matrices. A parallel analysis of bioaccumulation in Mediterranean and Antarctic samples is also presented. We used *M. galloprovincialis* and *V. philippinarum*, collected from the northern Adriatic coasts, and the Antarctic scallop *A. colbecki*, collected from Terra Nova Bay (Ross Sea, Northern Victoria Land) and stored in the Antarctic Environmental Specimen Bank, in order to compare the levels of PCB-11 in areas of high anthropogenic impact to those found in remote regions.

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DETERMINATION OF VOC AND HEAVY METAL IN CONDENSATES OF AIR COMPRESSED SYSTEMS BY HS-GCMS AND ICP-MS TECHNIQUES. A PROXY FOR THE ATMOSPHERIC AIR QUALITY CHARACTERIZATION?

S. Catania[1], E.E.Falcone[2], G. Franzino[1], F. Saiano[3]
[1]Laboratorio BROMATOS, Via Quinta Casa, 12 – 90142 Palermo.
[2]Dipartimento di Scienze della Terra e del Mare, Università degli Studi di Palermo, Via Archirafi, 22 - 90123 Palermo.
[3]Dipartimento di Scienze Agrarie e Forestali, Università degli Studi di Palermo, Viale delle Scienze ed. 4 – 90128 Palermo.

A compressed air system is composed by a compressor, which picks and compresses known volumes of atmospheric air. The presence of air contaminants such as dirt, moisture, oil, hydrocarbons gases and bacteria, depends on surrounding environment and it is a technological problem because they can aggressively attack, corrode and erode the piping system, controls, instruments and tools. Therefore, and even more so for sanitary use, they have strict requirements indicating where it should not be done his withdrawal. The contaminants problem is initially solved forcing compressed air to pass by a refrigeration dryer where it is cooled. The condensates, which are generated in the phase of compression, are separated and disposed of. These condensates could represent, although partially, an interesting proxy of atmospheric air quality in terms of organic and inorganic composition.
For these reasons, we have collected condensates of compressed air systems situated in different environment conditions, to test the above hypothesis.
The samples have been analyzed directly in headspace GC-MS for the organic volatiles compounds and in ICP-MS for the heavy metal and lanthanoids composition.
The obtained results were critically discussed based on the different amounts found.

A STERILIZATION PROCESS BASED ON γ RAYS: THE EFFECT ON WOODS

R. Cancelliere[1], C. Mazzuca[1], L. Micheli[1,2], M. Carbone[1,2], R. Lettieri[1], I. Bonacini[3], S. Prati[3], G. Sciutto[3], R. Mazzeo[3], L. Tositti[4], G. Ricci[5], D. Mostacci[5], A. Palleschi[1], G. Palleschi[1]
[1]Department of Chemical Sciences and Technologies, University of Rome "Tor Vergata" Via della Ricerca Scientifica, 00133 Rome, Italy
[2] Consorzio Interuniversitario Biostrutture e Biosistemi "INBB", Viale Medaglie d'Oro 305, 00136 Rome, Italy
[3] Microchemistry and Microscopy Art Diagnostic Laboratory (M2ADL), Department of Chemistry, University of Bologna - Ravenna Campus, via Guaccimanni 42, 48100 Ravenna, Italy
[4] Department of Chemistry, University of Bologna, via Selmi 2, 40126, Bologna, Italy
[5] Department of Industrial Engineering, University of Bologna, Via dei Colli 16, 40136 Bologna, Italy

Gamma ray sterilization is applied to verify? different products as medical material and gear - including more generally pharmaceuticals and cosmetics - and wooden craft products, e.g. musical instruments. The purpose of irradiating wood is to improve their shelf-life, destroying the living causes of decay: bacteria, fungi, worms and insects with their eggs and larvae. In general, gamma sterilization does not induce large changes in the chemical components of wood, or at least, no larger than other sterilization processes.
In this work, preliminary results are shown on chemical and structural effects of a sterilization experimental campaign in which increasing doses of gamma rays were delivered to four different types of wood: fir, maple, poplar and oak. The effects were evaluated comparing the results obtained with cyclic voltammetry, linear square voltammetry, and infrared spectroscopy techniques.
Furthermore, the surface products of wood degradation, and in particular of the degradation of cellulose and hemicelluloses, were investigated with a non-invasive method in which they were removed with gel of gellan. After that, electrochemical measurements were performed to detect glucose - one of the degradation products of polysaccharides - extracted by the application of the gel.
Results were compared to those attained from spectroscopic analysis, to reveal structural characteristics and possible presence of heavy metals.

Keywords: wood, sterilization, γ rays, spectroscopic and electrochemical measurement

SEASONAL DISTRIBUTION OF HEAVY METALS IN THE ANTARCTIC MARINE ENVIRONMENT: RELATIONSHIP WITH PHYTOPLANKTON

G. Libani, C. Truzzi, S. Illuminati, A. Annibaldi, G. Scarponi
Department of Life and Environmental Sciences, Università Politecnica delle Marche, via Brecce Bianche 60131 Ancona

Within the framework of the Italian Antarctic Programme, the partitioning of Cd, Pb and Cu between dissolved and particulate fractions, with particular attention to the algal particulate phase, was studied in the coastal waters of Terra Nova Bay (Western Ross Sea) during the austral summer 2013-2014. Seawater samples were collected in four periods from mid- November 2013 to early February 2014 at different depths of the water column. In order to relate the metal distributions with the physical and biological processes, master hydrographic variables were recorded during samplings. Metals were determined simultaneously by Square Wave Anodic Stripping Voltammetry (SWASV).
A seasonal decreasing trend of all the fractions was observed at the surface for each studied metal. During the season Cd was mainly present in its dissolved form, except at the maximum of fluorescence, where dissolved fraction was 60-70% of the total concentration.
Along the water column it showed a nutrient-type profile, with the algal particulate fraction varied from values below the detection limit up to ~20% of the total and up to ~100% of the total particulate fraction. Cu partitioning varied greatly during austral summer and it was affected by different factors not only phytoplankton activity.

CHARACTERISATION OF HISTORICAL MUSICAL INSTRUMENTS' MATERIALS BY PY/SPME/GC-MS WITH ON-FIBER SILYLATION

A.G. Rombolà[1], D. Fabbri[1], T. Rovetta[2], M. Malagodi[2,3]
[1] Department of Chemistry "Giacomo Ciamician", Università di Bologna, Campus di Ravenna, Via Sant'Alberto, 163 – 48123 Ravenna, Italy.
[2] Arvedi Laboratory of non Invasive Diagnostics, University of Pavia, via Bell'Aspa 3, 26100 Cremona, Italy.
[3] Department of Musicology and Cultural Heritage, University of Pavia, Corso Garibaldi 178, 26100 Cremona, Italy.

Historical stringed musical instruments are a group of artworks that in many cases are still used by famous musicians. Between the 17th and 18th centuries in Cremona (Italy), a group of violin makers, such as Amati, Guarneri and Stradivari, made instruments with extraordinary aesthetic and acoustic features. The analyses through scientific techniques performed on materials adopted in wood treatments and varnishes, could furnish new information about the past know-hows. In this research, some samples from a Nicola Amati (1596-1684) viola da gamba and a Jacob Stainer (1621-1683) cello have been collected, with the aim to characterize the organic compounds. Off-line pyrolysis with solid-phase microextraction of evolved products followed by on-fiber silylation and GC-MS was performed. This technique was developed for the analysis of anhydrosugars of diagnostic relevance in the characterisation of gums [1]. A small amount of sample of each musical instrument was pyrolysed at 600 °C for 100 seconds and products were trapped onto a CAR/PDMS SPME fibre. The on-fibre silylation was conducted by placing the fibre in the headspace of a 2 ml vial containing 50 µL of silylation agent (BSTFA/1%TMCS/10%pyridine) for 10 min. Products were thermally released in the injection port of a GC-MS system for their separation and identification. Derivatisation resulted quantitative as all the hydroxylated compounds were detected as persilyl ethers/esters. Products specific of hardwood lignin, guaiacol and syringol derivatives, were identified. In particular, their highly oxidised carboxylic forms principally in Stainer, could be characteristic of wood treatments. The presence of fatty acids in pyrolystaes was also confirmed by µFTIR analyses performed in transflection mode on the chloroform extracts. The identification of linoleic, suberic and azelaic acids suggested the use of siccative oils. Small levels of markers attributable to glue (pyrocoll) and diterpenic resins (dehydro and 7-oxo-dehydroabietic acids) were detected.

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RAW MATERIALS AND TECHNOLOGICAL CHANGES IN LIME MORTARS AND PLASTERS FROM EGNATIA IN THE ROMAN AGE

L.C. Giannossa[1], F. Mastrorocco[2], G. Eramo[3], G. Mastrocinque[4], M. Fornelli[2], A. D'Elia[3], A. Mangone[2]
[1]Department of Economics, Management and Business Law University of Bari Aldo Moro, Largo Abbazia Santa Scolastica 53, 70124 Bari (Italy)
[2]Department of Chemistry, University of Bari, Via Orabona 4, Bari (Italy)
[3]Department of Earth and Geoenvironmental Science, University of Bari, Via Orabona 4, Bari (Italy)

This study reports investigations on painted plasters and mortars from Egnatia. The investigations allowed to identify raw material and pigments and to reconstruct the technology employed in the manufacturing of painted plasters from the 2nd cent. BCE to 1st cent. CE. The pigments observed by Raman analyses highlighted Fe oxyhydroxide (*terre rosse*), cinnabar and hematite to obtain red colour, yellow ocher for yellow, charcoal for black, calcite for white, blue Egyptian for blue and glauconite (*terra verde*) for green. As concerns the technology, observations by optical and electronic microscopies showed that the pigments were fixed on the plaster still wet by the technique called "a fresco".
The same observations allowed also to point out the structural aspects of the supports of painted plasters. In most cases, supports are calcarenitic-type, characterized by fragments of spathic calcite, fossil and micritic limestones. Above the natural support, we observed plasters manufactured more or less accurately: in some cases the lime putty was mixed with well-selected material (crushed calcite with homogeneous particle size), in others not. The pigments appeared clearly penetrating the plaster.
Petrographical (OM), mineralogical (XRPD) and chemical (XRF) data suggest the use of the same limestone (Calcare di Bari formation) to produce lime through times, although the quality of lime putty is quite different.
While the bedding mortars were frequently prepared using littoral sand, in plasters of Imperial age it was observed the presence of spathic calcite only in the finishing layer, associated with preparation layers containing cocciopesto or littoral sand. The presence of straw in some preparation layers was probably aimed to delay the carbonatation, since the finishing layer with spathic calcite was applied.
Hydraulic mortars with cocciopesto are mainly present in the plaster stratification of the thermal baths, only in one sample is part of a floor.

CHEMICAL ANALYSES OF BURNT BONES: A FEASIBILITY STUDY WITH NON-DESTRUCTIVE TECHNIQUES

E. Dirminti[1], F. Cocco[2], M. Fantauzzi[2], C. Del Vais[1], A. Rossi[2]
[1]Dipartimento di Storia, Beni Culturali e Territorio, Università degli Studi di Cagliari, via Is Mirrionis 1 – 09123 Cagliari – Italy
[2]Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Campus di Monserrato S.S. 554 – Italy and INSTM, UdR Cagliari – Italy

This work aims to the study of the relevant aspects related to the chemical analysis of the burnt bones from the archaeological site of Tharros. This is one of the most important settlements during the Phoenician and Punic Periods in Sardinia. The first proper archaeological research in this area dates back to the 1950s, while in 1988-1991 and, more recently, in 2009-2013, in a joint mission with the University of Bologna, further explorations were carried out by the University of Cagliari. During the most recent excavations, the archaeological work documented a reasonable number of Phoenician burial pits, simply dug in the sandbank and sometimes covered with stone slabs, containing primary or secondary incineration remains and the corresponding funeral offerings[1]. The analysis of the cremains are being carried out within the frame of a PhD research project, aiming to the general understanding of the Phoenician necropolises of Oristano's area (central western Sardinia, Italy). The cremains will be also subject of an anthropological study to determine sex and age at death and the possible presence of double burials. These data will be possibly correlated with a certain typology of grave goods.
The analysis of the cremains is challenging, due to the heat-induced alterations on the bone, such as fragmentation, warping and shrinking. Toots and Voorhies[2] demonstrated that the concentration of zinc, strontium and lead could be used for the reconstruction of the food chain. The analyses at that time were carried out on the inorganic part of bones by atomic absorption spectroscopy.
Meanwhile, the topic has attracted the interest of some researchers but so far mainly destructive techniques have been used. In this presentation the results obtained by non-invasive and non-destructive analytical techniques, such as X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence (XRF), aiming to add archaeometric information to the investigation on samples of the cremains from Tharros, will be discussed and correlated to the archaeological context.

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EFFECTS OF CELLULOSE OXIDATIVE AND HYDROLYTIC DEGRADATION MONITORING BY INFRARED SPECTROSCOPY (ATR-FTIR) WITH APPROACH OF PRINCIPAL COMPONENTS ANALYSIS

A. Boaretto[1], C. Mazzuca[1], L. Micheli[1], A. C. Domakoski[1], A. Palleschi[1], G. Palleschi[1].
[1]Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00173 Rome, Italy

This study has the objective for control the degradation phenomena of the standard paper (Whatman paper, tipe 1) simulating the aging of the paper through artificial processes[1]:

- chemical oxidation with potassium periodate
- the acid hydrolysis with exposure to acid vapors hydrochloric acid
- and a mix of both treatments.

The artificial cellulose degradation was investigated by infrared spectroscopy in Fourier transform with attenuated total reflectance (FTIR-ATR), pH analysis. Principal components analysis (PCA) was used to analyze the data set of the results. All performed treatments were applied to significantly change the structure and properties of the paper, and the effects of deterioration, depending on the type of aging. The effects of aging was evaluated with the correlations between the structure of cellulose in good state and the formation of carboxyl and carbonyl groups after treatments, generating surface deformation up to breakage of the cellulose. Using the paper of oxidation index, defined as the ratio of integrals of bands at 1730 cm^{-1} to 1620 cm^{-1}, has been shown to be able to follow the degradation of cellulose in function of the treatment. The data were confirmed by other analytical characterization techniques, such High Pressure Liquid Chromatography (HPLC) and Field Emission Scanning Electron Microscopy (FE-SEM) used to study both the morphologic and topographic profile [2,3].

Keywords: Artificial aging; ATR-FTIR; pH e PCA.

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PALEO-ENVIRONMENTAL RECORD OF POLYCYCLIC AROMATIC HYDROCARBONS AND POLYCHLOROBIPHENYLS AT THE PERIPHERAL SITE GV7 IN EAST ANTARCTICA

R. Fuoco, S. Giannarelli, S. Francesconi, A. Ceccarini, C. Tiribilli, R. Spreafico
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via G. Moruzzi, 13 – 56124 Pisa

Today, human activities have altered the chemical composition of the environment and different classes of pollutants are ubiquitous because they are present in all environmental components, including the human being. A better understanding of changes in concentration of these substances in the environment on an appropriate time scale (paleo-environmental studies) plays an important role for the assessment of the possible sources of pollution, and for the quantification of their contribution to the pollution level, i.e. source apportionment evaluation.
In this work, we investigated the presence of Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorobiphenyls (PCBs), two classes of persistent organic pollutants (POPs), in a 50-m deep ice core sample collected during the XXIX Italian expedition at GV7 site in Antarctica. The evaluation of the concentration depth profile was obtained on the basis of the total concentration of 17 PAHs and 20 PCBs. The analysis of the ice core showed the presence of POPs in the atmosphere of the last century. The results highlight the diffusion of such pollutant also in a region that is considered one of the most uncontaminated in the world. Relevant concentration of PCBs were detected in the ice-sheets connected to the years of their production (1930-1990), showing the effective transportation of these compounds even to more remote areas. Besides the anthropogenic contribution, a provision of pollutants (especially PAHs) is due to epochal natural events. The high concentration of the analytes in conjunction with volcanic eruptions are in agreement with the dating of the ice core. More in general, the totality of the data obtained has allowed us to hypothesize an evident contribution for both classes of compounds due to natural events (eruptions) and a significant contribution due to the global transportation from the more industrialized areas. The decreasing trend noticed for PCBs is a considerable result, achieved through the implemented restriction. In fact, even though PAHs levels are growing, the higher toxicity, and hence the major 14 threat, is related to PCBs or to the PAHs with a higher molecular weight, that are present only in low percentages in our samples.

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A NOVEL APPLICATION OF ELECTROCONDUCTIVE PVA HYDROGEL TO EIS MEASUREMENTS FOR NON-INVASIVE AND NON-DESTRUCTIVE ANALYSIS ON ARCHAEOLOGICAL METALS

F. Di Turo[1], P. Matricardi[2], C. Cencetti[2], D. Zane[3], A. Curulli[3], R. Antiochia[2], F. Mazzei[2], G. Favero[2]
[1] Dipartimento di Scienze della Terra, Sapienza Università di Roma, P.le Aldo Moro 5, Roma, Italia, francesca.dituro@uniroma1.it
[2] Dipartimento di Chimica e Tecnologia del Farmaco, Sapienza Università di Roma, P.le Aldo Moro 5, Roma, Italia.
[3]Istituto per lo Studio dei Materiali Nanostrutturati, U.O.S. Sapienza Università di Roma, Via del Castro Laurenziano, 7, Roma, Italia.

Hydrogels are polymeric materials with a three-dimensional crosslinked structure that have been studies in several fields, such as pharmaceutical and biopharmaceutical, in biomedicine and biotechnology. Among hydrogels, Poly(vinyl alcohol) (PVA) is one of the most studied and applied in these disciplines thanks to several proprieties that this material shows. PVA has a relatively simple chemical structure with a pendant hydroxyl group. The preparation of PVA can be carried out by several methods, such as chemical cross linking and radiation induced cross linking (electron beam or gamma irradiation). A simpler mechanism of preparation is the freeze-thawing that involves "physical" crosslinking due to crystallite formation. Thanks to the repeated freezing and thawing cycles, aqueous PVA solutions can form crystallite and the number and stability of these crystallites increased as the number of freezing thawing cycles is increased. PVA hydrogels so obtained by repeated freezing-thawing are thermoreversible, shows mechanical strength, rubberlike elasticity, stability at room temperature, ability to retain their original shape and high water content.
Conductive PVA obtained by solution cast technique is studied thanks to its application possibilities' while conductive PVA obtained by freeze-thawing is not yet applied so far. On the other hand, among electroconductive hydrogels, PVA hydrogels is simple, it has low costs and it is health-safe for the operators especially if compared for example to polyaniline.
In the Cultural Heritage field, it was proposed the use of jellified electrolytes in order to ease electrochemical measurements *in situ* on metal artworks [1]. However, conventional jellifying agents (e.g. agar) show some mechanical limitations that can be overcome with PVA, building an appropriate electrochemical cell with this polymer.
In this work, we present the possibility to carry out EIS measurements with PVA prepared with a solution of NaCl and the freeze-thawing technique. The aim is to show that the use of PVA will allow to perform impedance measurements on bronze Roman coins, entailing the possibility to improve a

better system for non-invasive and non-destructive analysis on archaeological metals and explore the conservation conditions of different regions on all the metallic surface.

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MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS (VOCS) IN LIBRARIES AND ARCHIVES IN FLORENCE (ITALY)

A. Cincinelli[1], T. Martellini[1], A. Amore[1], L. Dei[1], G. Marrazza[1], E. Carretti[1], F. Belosi[2], F. Ravegnani[2], P. Leva[3]
[1]Department of Chemistry "Ugo Schiff" University of Florence – Via della Lastruccia, 3 – Sesto F.no, Florence (Italy)
[2] Institute of Atmospheric Sciences and Climate (ISAC), CNR, Via P. Gobetti, 101 – Bologna (Italy)
[3] European Commission, Joint Research Centre, Institute for Health and Consumer Protection (IHCP), Chemical Assessment and Testing Unit, Via E. Fermi 1, I-21020 Ispra (VA), Italy

Historical and modern libraries and archives house large numbers of book collections and documents made of a wide range of organic materials, including cellulose- (i.e. paper, some textiles wood), synthetic- (i.e. book, cover material) and other organic materials representing a minor amount of text-carrier (i.e. silk). They also house a large amount of writing/printing/drawing material (i.e. dies, inks, pigments, binders, glues) of which texts and images are produced. These materials undergo a continuous and inevitable deterioration due to natural ageing, or to contact with corrosive, oxidising, or acidic agents etc. Indoor air samples from libraries and archives in Florence, Italy, were collected and analysed for a variety of volatile organic compounds. The aim of the research was to perform a characterisation of the indoor air quality, and try to elucidate if there are VOCs that may cause or result from the determination of the cultural heritage institutions. All compounds of interest were regularly detected, with BTEXs (Benzene, Toluene, Ethylbenzene, Xylenes) being the most abundant and followed by cyclic volatile methylsiloxanes, aldehydes, terpenes and organic acids. The prevalence and qualitative characteristics, such as concentrations, profiles and indoor/outdoor ratios of BTEXs underline the important influence of the outdoor air infiltrations on the indoor air concentrations. Acetic acid that is a substance that can oxidise books and other exposed objects was detected at important concentrations (average concentrations ranged between 1.04 and 18.9 μg m^{-3}), while furfural, that is a known marker of paper degradation, was constantly present at concentrations that ranged between 5.26 and 32.6 μg m^{-3}.
This work shows the importance that indoor air quality monitoring campaigns can have in order to give early warning to cultural heritage institution managers about the impact that indoor air quality can have on exposed and/or preserved objects.

QUANTIFICATION OF ALIPHATIC AMINES IN THE AEROSOL PARTICULATE MATTER BY ION CHROMATOGRAPHY (IC)

A.Tinti [1], L. Corbella [1], P. Fermo [1], C. Colombi[2], E. Cuccia[2],V. Gianelle[2]
[1] Dipartimento di Chimica, Università degli Studi di Milano, 20133 Milano
[2] ARPA Lombardia, Milano, 20159

Amines are one of the most atmospherically-relevant organic compounds, being able to neutralize acids and to form toxic compounds. They are mainly present in the gaseous phase but they are partially converted into particulate phase after neutralization. The most common and abundant amines are the aliphatic low-molecular-weight [1]. More than one hundred of different molecules belong to this class; among them Ethyl-amine (EA), Methyl-amine (MA), Diethyl-amine (DEA), Trimethyl-amine (TMA) and Dimethyl-amine (DMA) are present with the highest concentrations. Till now different sources have been identified such as animal husbandry, agricultural activities, biomass burning, treatment of sewage and waste, combustion, industry, automobiles, cooking, tobacco smokes, composting operations and natural sources such as oceans, biodegradation of organic matter (that contains amino acids) and geologic sources [2]. The class of Methyl Amines is the most common in the atmosphere and has the highest concentrations near major sources, with a total global emission of 285 Gg N $year^{-1}$. TMA, the prevalent amine in the atmosphere, is estimated to have a global flux at approximately 170 Gg N $year^{-1}$, which is the highest among all alkylamines. It's believed that the majority of this flux comes from animal husbandry activities [2][3].
The main object of this study is the separation and quantification of aliphatic amines in PM10 samples collected in one urban site in Milan and in one rural site characterized by agricultural and zootechnical activities and placed in the southern part of Lombardy Region. The analysis of these species has been performed by IC (Ion Chromatography) [4].
After the set-up of the methodology, cromatography separation was achieved using a methanesulfonic acid (MSA) gradient elution on a Dionex CS17 column with conducibility suppressor (Dionex CSRS 500), which has allowed the quantification of the main cations as well.
The analytical results show higher concentration in the rural site than the urban one. In Milan a correlation between K^+/Levoglucosan and MA has been observed in the winter season allowing to state that one of the most important sources for this amine is biomass burning.
On the other hand, in the rural site an increase in the DMA's concentration (up to 36 ng/m^3) has been observed in early summer due to the use of pesticides (indeed DMA has a fungicide power and is employed in the formulation of pesticides). An increase of DMA has been observed in Milan both in early spring and in July. TMA concentration, mainly linked to husbandry activities, is higher in the rural site. These preliminary results have

authorize to put in evidence the presence in PM samples of this new class of potentially toxic compounds that up to now were not included among the substances commonly determined in the aerosol particulate matter.

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NEEDLE TRAP MICRO-EXTRACTION: AN INNOVATIVE APPROACH FOR THE ONE STEP SAMPLING AND PRE-CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN EXHALED BREATH

D. Biagini, T. Lomonaco, S. Ghimenti, F.G. Bellagambi, F. Di Francesco, R. Fuoco.
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via G. Moruzzi, 13 – 56124 Pisa

Over the last few years, breath analysis for monitoring metabolic disorders caused by specific diseases has become more and more attractive due to its non-invasiveness. Several approaches have been proposed for sample collection, preparation and analysis, aimed at the determination of various volatile organic compounds (VOCs). Needle Trap Device (NTD), a very promising tool, is a stainless steel needle (internal diameter 0.34 mm and length 6 cm) packed with different types and combinations of stationary phases. NTD allows sampling and analyte pre-concentration to be performed in a single step and combine the advantages of SPE (active adsorption) and SPME (small volume, direct injection in the GC inlet).
In this work, a mixture of 60 VOCs (i.e. aldehydes C3-C5, linear and branched ketones C4-C7, alcohols C1-C5) and other volatile compounds (e.g. pentane, acetone, isoprene, toluene and dimethyl disulfide) was used to optimize the analytical performances of NTDs packed with DVB (1 cm, 80/100 mesh), Carbopack X (1 cm, 60/80 mesh) and Carboxen 1000 (1 cm, 60/80 mesh) by GC-MS/MS analysis. In particular, the effect of the humidity level on the desorption process has been assessed and the relationship between desorption efficiency and sample relative humidity (RH%) evidenced. For the first time, the use of a labeled internal standards mixture was proposed to correct the effect of the humidity level on the chromatographic signal. In addition, different extraction parameters (sampling flow rate and sample volume), desorption conditions (desorption time and GC inlet temperature), as well as the carry over effect and the recovery after sample storage at room temperature, were optimized.
The measurements were carried out using water-saturated standard mixtures of the 60 VOCs, at a relative humidity level comparable to exhaled breath (RH 90%). NTDs were automatically desorbed by a CONCEPT GC-autosampler (PAS Technology) and VOCs were analyzed by a 7890B GC System coupled to a 7010 MS Triple Quad mass spectrometer (Agilent Technologies).

Acknowledgement. This work was supported by the project PHC-643694 HEARTEN, funded by the European Commission under the H2020 programme.

ARCHAEOMETRIC STUDY ON APULIAN RED FIGURE VASES OF INTESA SANPAOLO COLLECTION

F. Mastrorocco[1], L.C. Giannossa[2], S. Di Leone[1], R. Laviano[3], M. Pallara[3], I.M. Muntoni[4], F. Giacobello[5], A. Mangone[1]
[1]Department of Chemistry, University of Bari, Via Orabona 4, Bari (Italy)
[2]Department of Economics, Management and Business Law University of
ly)
[3]Department of Earth and geo-environmental sciences, University of Bari, Via Orabona 4, Bari (Italy)
[4]Superintendence for Archaeological Heritage of Puglia, Via De N ittis, 7, Foggia (Italy)
[5]Department of Cultural Heritage and Environment, University of Milano, Via Festa del Perdono 7, Milano (Italy)

An archaeometric study on Apulian red figure pottery from the collection "Giuseppe and Francesco Caputi", composed of vases recovered between 1830 and 1860 in Ruvo di Puglia (Central Apulia), has been carried out. Nowadays, the collected artworks are owned by Intesa Sanpaolo and exhibited in Vicenza (Italy) at Gallerie d'Italia. The aim of the research was identifying the provenance of the raw materials and the production technology used.
In particular, vases stylistically attributed to Pittore di Baltimora, Pittore della Patera, Pittore di Licurgo and workshop of Pittore di Dario and Pittore dell'O ltretomba have been analyzed.
A chemical- mineralogical characterization of ceramic bodies by ICP-MS, MO, SEM-EDS and XRD analyses has been performed. As regards the chemical analyses, a few micrograms of clay scraped off from hidden areas of the vases - inside or under the base - has been carried out using a method that does not damage the archaeological vases already exposed and valued in museum contexts, whereas, for the minero-petrographic analyses performed by OM, SEM-EDS and XRD, slivers of few square millimeters wide have been removed from pre-existing vase cracks.
Also, a statistical multivariate analysis has been performed on the chemical compositional data: vases from the collection, red figure pottery certainly coming from Apulia and material attributed to the same painter or workshops. The overall results made it possible to hypothesize the production centers of the findings.
Moreover, defining the mineralogical composition of the archaeological materials made it possible to answer to technological questions relating to ancient ceramic's production processes and potential changes in manufacturing techniques (the firing temperature, the duration of the process, the red/ox atmosphere in kilns, etc), as well as reconstruct XIX cent. AD restoration actions of the red figure samples analyzed.

PEROVSKITE FOR THE HIGHLY SELECTIVE ENRICHMENT OF PHOSPHOPEPTIDES

A.L. Capriotti, C. Cavallo, C. Cavaliere, F. Ferraris, S. Piovesana, R. Zenezini Chiozzi, A. Laganà
Dipartimento di Chimica, Università degli Studi di Roma "La Sapienza", Piazzale Aldo Moro, 5 – 00185 Roma

Protein phosphorylation, one of the most important posttranslational modifications, is involved in many cellular processes, including proliferation, differentiation and apoptosis . Abnormal phosphorylation is commonly associated with various diseases, such as cancer and metabolic disorders [1]. Therefore, the identification and quantification of protein phosphorylation are necessary to elucidate their functions and useful for diseases diagnostics and therapeutics. Mass spectrometry (MS) based techniques have become the foremost choice for phosphoproteomics analysis because of their high sensitivity and accuracy. Up to date, various methods have been developed for phosphopeptide enrichment, and metal oxide affinity chromatography (MOAC) using TiO_2 is one of the most powerful and widely used approaches. In this work, the high selectivity of $CaTiO_3$ was demonstrated. Ordered mesoporous $CaTiO_3$ perovskites were synthesized under different conditions in order to obtained materials with different physical properties such as pore diameters, specific surface area, pore size distribution and electrophilic abilities. Characterization of the synthesized materials was carried out through several techniques, such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and BET analysis.
The performance of the four different type of synthesized $CaTiO_3$ perovskites were compared in the enrichment of phosphopeptides from tryptic digest of yeast cell lisates.
Different sample to phase ratios were tested to maximize the selectivity of the protocol.
All enrichment methods were developed embedding the protocol in a typical shotgun proteomics workflow, comprising nanoHPLC, high resolution mass spectrometry and bioinformatics data analysis, for performance evaluation and comparison to established methods.
Our result showed they has very good performance with the enrichment specificity of 50% for phosphopeptides. Therefore, $CaTiO_3$ may be a promising and alternative material for phosphopeptide enrichment in large-scale phosphoproteomics study.

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LABEL FREE PROTEOMIC ANALYSIS OF CACO2 CELLS EXPOSED TO SIMULATED MICROGRAVITY

A. L. Capriotti[1], C. Cavaliere[1], F. Ferraris[1], G. La Barbera[1], E. Michelini[2], R. Zenezini Chiozzi[1], A. Roda[2], A. Laganà[1]
[1]Dipartimento di Chimica, Università degli studi di Roma "La Sapienza", Piazzale Aldo Moro, 5 – 00185 Roma
[2]Dipartimento di Chimica "G. Ciamician", Università di Bologna-Alma Mater Studiorum, Via Selmi, 2 - 40126 Bologna

Without a doubt, space is one of the most exciting and dangerous environments. In addition to increasing our fundamental knowledge in all fields of the life sciences, space biology promotes research aimed at preserving human health and well-being, as well as designing life-regenerative support systems to foster habitability and sustainability in space. Space is a hostile environment characterized by high vacuum, temperature extremes, meteoroids, space debris, ionospheric plasma, microgravity, ultraviolet and ionizing radiation, which all represent risks for human health [1]. Hence, it is clear that a deep understanding of the biological consequences of exposure to the space environment is required to design efficient countermeasures to minimize their negative impact on astronauts. While properly designed spacecraft and spacesuits could mitigate some immediate risks, space radiation and negligible gravity cannot be completely avoided. Among the alterations that might occur, changes in the gastrointestinal (GI) apparatus and related gut inflammatory states are of particular relevance. Microgravity could lead to decreased GI motility and reduced dietary intake [2]. Such possible alterations must be detected to take the necessary measures to avoid negative consequences to the crewmembers' health. To investigate microgravity effect on GI motility human colon adenocarcinoma cells (Caco-2) were selected as model of the intestinal barrier. Considering the biological effects that microgravity could have on protein expression, we compared protein profiles of Caco-2 cells grown in simulated microgravity and in normal gravity conditions. Caco-2 cells were exposed for 48 and 72 hours to microgravity conditions using Rotary Cell Culture System (RCCS-1-HARV, Synthecon). The resultant 4 conditions (cells grown for 48 and 72 hours with normal gravity and with microgravity) were replicated 3 times to take in consideration any possible biological variability. All the twelve different samples were lysed in urea buffer, quantified by Bradford assay, digested with trypsin and fractionated by HPLC. We used a basic pH fractionation because it has proven to have a good orthogonality with subsequently reverse phase chromatography [3]. Twelve fractions were collected in the first off-line dimension and subsequently analyzed with nano-liquid chromatography-tandem mass spectrometry. The resulting 12 raw files were processed with MaxQuant software, setting an FDR of 1% both for PSM and proteins. All

the resulting data were analyzed with statistic programs like Perseus or R. The qualitative and quantitative study of the protein global responses to perturbations, allowed the investigation of the regulatory molecular mechanisms of GI motility and inflammatory states process.

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MEPS-HPLC-PDA ASSAY FOR CIPROFLOXACIN AND LEVOFLOXACIN IN HUMAN CYSTIC FIBROSIS PATIENTS SPUTUM DETERMINATION

E. De Luca[1], G. Bellagamba[1], M. Locatelli[1], M.T. Ciavarella[1], R. Cifelli[1], C. Celia[1], L. Di Marzio[1], R. Grande[1], M.C. Cristiano[2], D. Paolino[3]
[1]University "G. d'Annunzio" Chieti-Pescara, Department of Pharmacy, 66100, Chieti-Italy; E-mail: marcello.locatelli@unich.it
[2]Dipartimento di Scienze della Salute, Università di Catanzaro "*Magna Graecia*", Viale "S. Venuta", 88100 Catanzaro
[3]Dipartimento di Medicina Clinica e Sperimentale, Università di Catanzaro "*Magna Graecia*", Viale "S. Venuta", 88100 Catanzaro

This work [1] reports a MEPS–HPLC–PDA assay for the simultaneous analysis of ciprofloxacin and levofloxacin in sputum samples collected from cystic fibrosis (CF) patients. The FLQs were resolved on a Discovery C8 column (250 mm × 4.6 mm; 5 μm) under isocratic conditions in 15 min. The method was validated over concentrations ranging from 0.05 to 2 μg/mL for both analytes in human sputum, and enrofloxacin was used as internal standard.
The MEPS–HPLC–PDA method was validated using biological samples collected from CF patients orally or intravenously injected with FLQs.
The resultant data showed that the method is selective, sensitive and robust over range of concentrations for both FLQs. The limit of quantification of the method was 0.05 μg/mL for both analytes with a good linearity up to 2 μg/mL. The intra- and inter-day precision (RSD%) values were ≤10.4% and ≤11.1%, respectively, for all range of analysis. The intra- and inter-day trueness (Bias%) values are ranged from−11.8% to 7.25% for both antibiotic drugs.
This is the first MEPS–HPLC–PDA based method that uses MEPS procedure for simultaneous determination of ciprofloxacin and levofloxacin in human sputum.
The method was tested successfully on real sputum samples by following a conventional drug administration. Furthermore, the MEPS–HPLC–PDA based method provides more advantages to detect and analyze quickly the antibiotic drugs in biological matrices than other analytical procedures reported in literature.

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MEPS-HPLC-PDA DETERMINATION OF TWELVE AZOLES DRUGS IN HUMAN PLASMA AND URINE

E. De Luca[1], M. Locatelli[1], G. Bellagamba[1], D. Rampino[1], M. Petrocco[1], A. Tartaglia[1], D. Paolino[2,3], C. Celia[1,4], R. Grande[1,5], R. Cifelli[1], G. Zengin[6], L. Di Marzio[1], S. Carradori[1]
[1]University "G. d'Annunzio" Chieti-Pescara, Department of Pharmacy, 66100, Chieti-Italy; E-mail: marcello.locatelli@unich.it
[2]University of Catanzaro "Magna Graecia"; Department of Clinical and Experimental Medicine; Viale "S. Venuta"; 88100 Catanzaro; Italy.
[3]University of Catanzaro "Magna Græcia"; Inter-Regional Research Center for Food Safety & Health, Viale "S. Venuta"; 88100 Catanzaro; Italy.
[4]Houston Methodist Research Institute; Department of Nanomedicine; Houston; Texas 77030; USA.
[5]Center of Excellence on Ageing, "G. d'Annunzio" University Foundation; Via L. Polacchi 11; 66100 Chieti; Italy.
[6]Selcuk University; Department of Biology; Konya; Turkey.

This work [1] reports a MEPS-HPLC-PDA procedure for the simultaneous analysis of twelve azoles, commonly used for the treatment of several systemic fungal infections.
The azoles, were resolved on a Luna C_{18} column with a run time of 36 minutes, without further purification and re-equilibration comprised. The method was validated over concentrations ranging from 0.02 to 5 μg/mL both in human plasma and urine.
The method was successfully tested to detect these azoles in plasma and urine collected from healthy volunteers after single dose administration. The results indicate that the assay is selective, and sensitive over range of concentrations for all the analytes. The intra- and inter-day precision (RSD%) and the intra- and inter-day trueness (Bias%) values are fulfill with ICH requirements for all azole drugs.
This is the first MEPS-HPLC-PDA based assay that uses MEPS procedure for simultaneous determination of all these analytes in human plasma and urine.

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TGA/CHEMOMETRICS AS A NEW DIAGNOSTIC TOOL METHOD APPROACH FOR β-THALASSEMIA SCREENING

G. Gullifa[1], R. Risoluti[1], P. Caprari[2], F. Sorrentino[3], S. Materazzi[1]
[1]Dipartimento di Chimica, "Sapienza"- Università di Roma, P.le A. Moro 5-00185 Roma
[2]Dipartimento di Ematologia, Oncologia e Medicina Molecolare, Istituto Superiore di Sanità, viale Regina Elena 299-00161 Roma
[3]UOS DH - Talassemia, Ospedale S. Eugenio, P.le dell'Umanesimo, 10-00144 Roma

β-Thalassemia belongs to the class of hemoglobinopathies. It is characterized by the reduced or absent synthesis of the β-globin chains of the adult hemoglobin (HbA), with consequent reduction in the synthesis of hemoglobin (Hb), red blood cells (RBC) and anemia. Hematological clinical overview allows to distinguish three main forms: β-Thalassemia major, intermedia and minor (e.i. the carrier state).
β-Thalassemia is one of the most widespread forms of hereditary blood disorders. For this reason, the need to develop quick and effective techniques for screening and diagnosis of β-Thalassemia is growing. A new bioanalytical approach for a early detection of β-Thalassemia, based on Thermogravimetric Analysis and Chemometrics, has been proposed.
The Thermogravimetric Analysis has been applied on whole blood samples from healthy subject and β-Thalassemic subject. The Principal Component Analysis has been used to investigate and correlate thermogravimetric profiles. Outcomes show different thermogravimetric profiles among two populations examined because of different amount of water content and corpuscular fraction and the breakdown between free and bound water has been considered the diagnostic parameter for β-Thalassemia.
To validate the proposed approach and confirm the presence or absence of pathology, the same samples have been submitted to Blood Count and in particular, for the diagnosis of β-Thalassemia have been evaluated Hemoglobin content (HGB), Hematocrit (HCT), Red Blood Cells (RBC), Mean Corpuscular Volume (MCV), Mean Corpuscular Hemoglobin (MHC) and Red-cell Distribution Width (RDW).
This preliminary and promising study allows to consider coupled TGA/Chemometrics an alternative, cheap and fast diagnostic method for screening of β-Thalassemia.

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TOWARDS A FLOW-INECTION IMMUNOASSAY FOR SAXITOXIN DETERMINATION IN SEA WATER

L. Micheli[1,2], A. Sarra[1], M. Ottviani[1], S. Felici[1], G. Palleschi[1,2]
[1]Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", via della Ricerca Scientifica, 00133 Rome, Italy
[2]Consorzio Interuniversitario Biostrutture e Biosistemi "INBB", Viale Medaglie d'Oro 305, 00136 Rome, Italy

Saxitoxin (STX) is one of the most lethal non-protein toxins (LD_{50} 9 μg Kg^{-1}) and is the only marine natural product that has been declared chemical weapon. Contamination of shellfish with STX has been associated with harmful algal blooms throughout the world [1]. STX has the ability to bioaccumulate up trophic levels. Ingestion of infected marine organisms, by humans, induces a lethal disease known as Paralytic Shellfish Poisoning (PSP) that is currently without antidote or detoxification pathway. This family of toxins acts blocking the sodium channels on cells and cause very serious symptoms varying from a slight tingling sensation to fatal respiratory paralysis. The maximum tolerance levels, as established by the European Union and according with the Food and Drug Administration, refer to 40 - 80 μg PSP *x* 100 g edible portion of fresh, frozen or tinned shellfish [2].
Presently, laborious and expensive mouse assay and HPLC methods are used to detect the presence of STX in fish [3]. The goal of this work is based on a flow injection immunoassay system (FI-IA) with colorimetric detection. The method consists in an off-line incubation of the sample containing STX (Ag) with fixed amounts of anti-STX antibody (Ab) and STX labelled with peroxidase (Ag*) until the equilibrium is established. In this mixture, a competition between Ag and Ag* for the Ab occurs. The mixture is then injected into a flow system where the separation of the free Ag* and the antibody-bound tracer (AbAg*) is performed in a column with immobilized protein G. In the column all the antibodies due to the protein G affinity for the constant (Fc) of the antibody are retained. The activity of the enzyme labelled Ag* is measured spectrofotometrically using the TMB substrate (ready to use).
The immunoanalytical system was optimised, characterised, and compared with those obtained with commercial ELISA kit.

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EFFECT OF TEMPLATE LATE ADDITION ON THE BINDING PROPERTIES OF MOLECULARLY IMPRINTED POLYMERS

C. Baggiani, G. Spano, C. Giovannoli, V. Maurino, L. Anfossi
Dipartimento di Chimica, Università degli Studi di Torino, Via Giuria, 5 – 10125 Torino

In the non-covalent molecular imprinting approach, the use of pre-polymerized functional macromonomers – freely dissolved in a porogenic solvent or grafted onto a solid surface – greatly increases the stability of the complex between the template molecule and the forming cross-linked polymer, with a net gain in terms of binding properties. The cross-linking process of such macromonomers can be considered somewhat similar to the change of state from a microgel solution to a solid polymer that happens during the process of bulk polymerization. On this basis, we hypothesized that the late addition of a template molecule to a mixture of functional monomers and cross-linkers during the polymerization process can enhance the binding properties of the final bulk polymer.
To verify this hypothesis we chose to imprint a series of bulk polymers with a well-known template, diclofenac, by using a polymerization mixture in acetonitrile (4-vinylpyridine / 2-hydroxyethylmethacrylate / divinylbenzene 2+2+5 mol/mol) previously developed in our laboratory, but adding the template progressively later respect to the starting of the thermopolymerization process. The experimental conditions were chosen after a preliminary study of the polymerization process, designed to determine the speed of gelling according to the polymerization temperature. After the polymerization, the imprinted and non imprinted bulk materials were crushed, sieved and packed in 50x2 mm HPLC columns and the binding parameters in acetonitrile (affinity constant and binding site density) for the template molecule diclofenac and a related ligand, mefenamic acid, were determinated by frontal chromatography.
From the analysis of the experimental data, it results that the initial hypothesis is verified, as the imprinted polymers prepared by late addition (delay time of 10-40 minutes) of the template show a higher binding affinity with respect to the reference polymer prepared in the presence of template from the beginning, with a decreasing trend with respect to the increase of delay time. Moreover, no significant effects were noted on the selectivity of polymers. The applicability of this approach to the imprinting of templates in polar media will be discussed according to the preliminary results obtained.

NANOPOROUS FUNCTIONALIZED GOLD FOR SERS-BASED IMMUNOSENSING

C. Giovannoli, F. Turci, P. Rizzi, L. Anfossi, A. Damin, S. Bordiga, C. Baggiani
Dipartimento di Chimica, Università degli Studi di Torino, Via Giuria, 5 – 10125 Torino

Health promotion and disease prevention are included in the most important challenges of Horizon2020. Thus, the development of diagnostic tools based on sensible and selective analytical approaches can be of significant importance for the development of boosting cutting-edge biotechnologies as future innovation drivers and they can be of crucial importance for helping biotech industry to stay at the front line of innovation. Main fields of interest mainly concern the set-up of devices based on accessible and affordable detection of pathogenic agents, disease markers, food contaminants or environmental toxicants. As alternative to the traditional enzyme-linked immunosorbent assay (ELISA) that is considered a gold standard for routine and target-driven analysis, more recently a lot of efforts have been dedicated to develop fast quantitative lateral flow immunoanalysis (LFIA) devices for rapid point-of-care testing (POCT), even though not always competitive with ELISA in terms of sensitivity and robustness.
The interest for nanoporous gold (NPG) is increasing due to the relatively simple synthesis techniques and its structural, morphological and chemical flexibility. NPG can be modified with functional groups allowing a broad range of possible applications in the analytical field. Here, we present the preliminary studies related to the development of a new sensing strategy based on the coupling of analytical antibodies with NPG. This approach aims to synergistically exploit the high selectivity of antibodies and the single-molecule sensitivity of surface enhanced Raman spectroscopy (SERS), for the versatile detection of target compounds, ranging from low mass organic molecules to large proteins. In order to preliminary assess the ability of NPG of different porosity and morphology to be covalently functionalized with a anti-human serum albumin antiserum (pAb anti-HSA), two different synthetic routes were considered. The first one was based on the preliminary gold functionalization with mercaptoalkyl/arylamines or mercaptoalkyl/arylacids and the subsequent immobilization of the immunoglobulins on the pAb anti-HSA monolayer via carbodiimide/NHS eaction. The functionalized gold surfaces were tested by using a HRP-labelled anti-rabbit antiserum in order to assess the binding behaviour. Preliminary results shows the effective validity of NPG as reactive support indicating the feasibility of the present approach.

EXPLOITING QUANTUM DOTS FOR SENSITIVE AND STRAIGHFORWARD DETECTION IN IMMUNOCHROMATOGRAPHIC STRIP TESTS

L. Anfossi[1], F. Di Nardo[1], C. Giovannoli[1], G. Spano[1], I.Y. Goryacheva[2], V.V. Goftman[2], C. Baggiani[1]
[1]Dipartimento di Chimica, Università degli Studi di Torino, Via Giuria, 5 – 10125 Torino
[2]Department of General and Inorganic Chemistry, Chemistry Institute, Saratov State University, Saratov (Russia)

The immunochromatographic strip test (ICST), also known as lateral flow immunoassay, offers several advantages when compared to other immunoanalytical methods, such as: stand-alone format, rapid detection, no requirements for technical expertise and laboratory equipment, and low cost. It is thereby considered as particularly feasible for using outside the laboratory. Traditional ICSTs employ gold nanoparticles (GNPs) to generate visual signals and usually provide a binary yes/no answer in accordance with a specific or mandatory cut-off level. However, new labels leading to improved sensitivity and allowing for quantitative detection are strongly demanded. Among fluorescent probes, quantum dots (QDs) have attracted the interest of the biosensing community due to their unique luminescent properties; such as high quantum yields, size-tunable fluorescence, broad absorption spectra, narrow and symmetric emission spectra, and high resistance to photobleaching. In particular, ICSTs exploiting QD have been successfully developed and the use of QDs compared to GNP allowed improving sensitivity and precision of the ICST significantly [1]. More interestingly, QDs fluorescence is quenched by resonant energy transfer to nanoparticles of suitable materials when these are kept at a convenient distance, i.e.: the distance achieved by antibody-antigen complex formation. We exploited this feature to design a new ICST format for small molecules detection, in which the Test reagent on the analytical membrane comprised the QD-labeled antigen, while the GNP-labeled antibody flowed across the membrane. In our original design the analytical signal is the QD fluorescence detectable on the Test line. Thus, a negative sample, which causes the GNP-labeled antibodies binding to the QD-labeled antigen, switches-off the signal, contrarily to what happens for standard ICSTs for small molecules. Instead, the positivity turns-on the QD luminescence on the Test line, allowing for straightforward interpretation of the test result. The presentation would demonstrate the feasibility of the proposed approach by applying the ratiometric fluorescent ICST for the sensitive detection of beta-lactams in milk.

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CHARACTERISATION OF DIFFERENT MONOCLONAL ANTIBODIES RAISED AGAINST HAZELNUT PROTEIN EXTRACT

F. Di Nardo[1], K. Lauter[2], L. Anfossi[1], C. Baggiani[1], S. Baumgartner[2]
[1]Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria, 5 – 10125 Torino
[2]Department für Agrarbiotechnologie, Universität für Bodenkultur Wien, Konrad-Lorenz-Straße, 20 – 3430 Tulln an der Donau

Allergic reactions caused by food consumption are an increasing disease among the total population worldwide. For those affected by food allergy, consumption of normally nutritious foodstuffs, even in small quantities, can produce life-threatening adverse reactions.
Hazelnut (*Corylus avellana*) is in the top list of major food allergens: allergy to hazelnut is one of the more widespread tree nut allergies, with allergic reaction ranging from mild symptoms to more severe reactions [1].
The only current "therapy" remains strict avoidance of foods to which the individual is sensitised. This troubling situation leaves patients at risk from accidental exposure when foods are either cross-contaminated with allergenic food, or simply incorrectly described or labelled. Therefore, reliable and highly sensitive analytical methods are needed to be developed for control and labelling of food ingredients and products.
Most current allergen detection methods are immunoassays, utilising antibodies raised against the target food or food protein extracts to broadly identify the allergenic food.
Food allergens are food ingredients which contain a mixture of proteins. These proteins consist of allergenic and non-allergenic proteins; therefore, to develop methods that measure representative proteins, which are carried out by immunization process, is important to know which antigen the antibody recognises.
We characterised different homemade monoclonal antibodies (mAbs) raised against the whole hazelnut protein extract, in order to understand which antigen/s they recognise. Knowing which antigens are recognised, can allow a precise use of the mAbs to develop hazelnut allergens detection systems.
In the development of detection methods, mAbs are often preferred to polyclonal antibodies because of their specificity (they are less susceptible to cross-reactivity) and especially for their permanent availability.
The methods applied for the mAbs characterisation and the obtained results will be discussed in this communication.

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DETERMINATION OF WARFARIN AND ITS ACTIVE METABOLITES IN DRIED BLOOD SPOTS BY UHPLC-ESI-MS/MS

S. Ghimenti[1], T. Lomonaco[1], D. Biagini[1], F. G. Bellagambi[1], M. Onor[2], L. Ruocco[3], G. Pellegrini[3], M. G. Trivella[4], F. Di Francesco[1], R. Fuoco[1]
[1]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via G. Moruzzi, 13 – 56124 Pisa
[2]Istituto di Chimica dei Composti Organometallici, Consiglio Nazionale delle Ricerche, Via G. Moruzzi, 1 – 56124 Pisa
[3]Laboratorio di Analisi Chimico-Cliniche, Azienda Ospedaliera Universitaria Pisana, Via Paradisa, 2 – 56125 Pisa
[4]Istituto di Fisiologia Clinica, Consiglio Nazionale delle Ricerche, Via G. Moruzzi, 1 – 56124 Pisa

Warfarin (WAR) is the most common oral anticoagulant drug prescribed for the treatment of many diseases (e.g., atrial fibrillation and pulmonary embolism). The narrow therapeutic index coupled with the large individual variability of response to treatment and the delayed anticoagulant effect of WAR (<72 hours) pose serious risks of hemorrhagic events or thrombi formation if WAR dose is not correctly balanced. Thus, the effectiveness and safety of the therapy must be frequently controlled by monitoring the International Normalized Ratio (INR) and adjusting the WAR dose accordingly. An interesting alternative to the INR assay could be the determination of WAR and its active metabolites (Warfarin alcohols) in blood as it was previously demonstrated that a good correlation exists between these two parameters.
The aim of this study was to develop an analytical procedure for the determination of WAR and its metabolites in Dried Blood Spots (DBSs) by Ultra High Performance Liquid Chromatography combined with tandem Mass Spectrometry (UHPLC-ESI-MS/MS). DBSs represent a convenient strategy for drug therapeutic monitoring, especially when blood samples must be collected frequently. DBS samples were produced by pipetting 10 µL of blood sample (collected from fifteen patients undergoing WAR therapy) on Whatman 903 filter papers. The resulting spots were dried at room temperature for at least two hours. The analytes were then extracted from a 6 mm DBS punch using 500 µL of a methanol-acetonitrile mixture (3:1 v/v) and diluted 1:4 with an aqueous solution of 0.1% formic acid prior to LC-MS analysis.
The analytical figures of merit highlighted the reliability of the proposed method for the determination of WAR and Warfarin alcohols in DBS samples. Good correlations between the concentration of both analytes measured in patient DBS and plasma samples were found, confirming the possibility of using DBSs for monitoring the WAR concentrations in blood.

DETERMINATION OF ALDOSTERONE, CORTISOL, AND 8-ISO-$PGF_{2\alpha}$ IN ORAL FLUID SAMPLES BY UHPLC-MS/MS

F.G. Bellagambi[1], S. Ghimenti[1], T. Lomonaco[1], D. Biagini[1], F. Di Francesco[1], M.G. Trivella[2], M. Marzilli[3], R. Fuoco[1]
[1]Dipartimento di Chimica, Università di Pisa, Via Giuseppe Moruzzi, 13 – 56124 Pisa
[2]Istituto di Fisiologia Clinica, Consiglio Nazionale delle Ricerche, Via Giuseppe Moruzzi, 1 – 56124 Pisa
[3]Dipartimento di Patologia Chirurgica, Medica, Molecolare e dell'Area Critica, Università di Pisa, Via Paolo Savi, 10 – 56126 Pisa

Aldosterone is an endogenous mineral corticosteroid whose primary physiological function is to regulate both the metabolism of sodium and potassium ions, and the volume of extracellular fluid and blood pressure. Similarly, cortisol is known to unfavorably affect classic cardiovascular risk factors such as hypertension and insulin resistance. Isoprostanes such as 8-iso-$PGF_{2\alpha}$ are a unique series of prostaglandin-like compounds and reliable markers of lipid peroxidation, and consequently of oxidative stress, whose pathophysiologic role in HF is well established.
Due to their role in the pathogenetic mechanism, and since their levels in oral fluid are correlated with the free amounts in blood, the non-invasive measurement of aldosterone, cortisol and 8-iso-$PGF_{2\alpha}$ in oral fluid may be a useful tool for monitoring patients affected by heart failure.
In this work, the development and validation of an analytical procedure for the determination of aldosterone, cortisol, and 8-iso-$PGF_{2\alpha}$ by UHPLC-MS/MS in a single chromatographic run is described. An optimized liquid-liquid extraction procedure and the influence of sampling parameters such as oral fluid flow rate and pH on the concentrations of analytes are also presented.

Acknowledgement: This work was supported by the project PHC-643694 HEARTEN, funded by the European Commission under the H2020 programme.

QUANTIFICATION OF OCHRATOXIN-A IN WINE: A SMARTPHONE-BASED DEVICE FOR ULTRASENSITIVE CHEMILUMINESCENT-LATERAL FLOW IMMUNOASSAY

M. Zangheri[1], M. Mirasoli[1], L. Anfossi[2], F. Di Nardo[2], C. Giovannoli[2], M. Guardigli[1], C. Baggiani[2], A. Roda[1]
[1]Dipartimento di Chimica "Giacomo Ciamician", Alma Mater Studiorum-Università di Bologna, Via Selmi, 2 - 40126 Bologna
[2]Dipartimento di Chimica, Università di Torino, Via Giuria 5-10125, Torino

Ochratoxin A (OTA) is a mycotoxin produced by several species of *Aspergillus* and *Penicillium* fungi that is detected worldwide in various food and feed sources. Since OTA represents a potential hazard for human health, the European Community (EC) has established a maximum level for OTA in various feed and foods, in particular 2 μg L^{-1} in grape juices, wine and must. 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 multiplex detection of type-B fumonisins and B1 aflatoxin in maize samples based on a chemiluminescence Lateral Flow ImmunoAssay (CL-LFIA) coupled with a portable ultrasensitive CCD-based "contact" imaging device [1]. 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.
Here, we report on the development of a smartphone-based simple, rapid and accurate biosensor based on CL-LFIA method for quantitative detection of OTA in wine. The biosensor is based on a direct competitive immunoassay using peroxidase (HRP)-OTA conjugate, which is detected by adding the CL substrate luminol/enhancer/hydrogen peroxide and by using a smartphone camera for the image acquisition and data handling [2].
A self-standing microfluidic cartridge was developed, which houses the LFIA membrane and all the reagents necessary for the analysis and that can be easily coupled with the smartphone camera to perform CL measurements in an integrated device. The developed system is suitable for the quantitative analysis of OTA in wine samples with limits of detection that comply with EC legislation.

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AN ORIGAMI PAPER-BASED CHEMILUMINESCENCE BIOSENSOR FOR GLUCOSE

M. Guardigli[1], M. Mirasoli[1,2], M. Zangheri[1], D. Calabria[1], C. Caliceti[1], A. Roda[1,2]
[1]Dipartimento di Chimica "Giacomo Ciamician", Alma Mater Studiorum – Università degli Studi di Bologna, Via Selmi, 2 - 40126 Bologna
[2]Consorzio Interuniversitario INBB, Viale delle Medaglie d'Oro, 305 - 00136 Roma

The development of Point-of-Care (POC) analytical devices for diagnostic applications is an ever growing field of research. In this context, paper-based microfluidics is emerging as a very promising approach for the development of disposable, easy-to-use, rapid and cost-effective devices, while the exploitation of the origami concept allows convenient translation of multistep analytical procedures.
We have developed a portable paper-based analytical device for the measurement of glucose that combined the glucose oxidase-catalyzed enzyme reaction for the production of hydrogen peroxide from glucose and the luminol-hexacyanoferrate(III) chemiluminescent system for its detection. The use of paper as analytical support allowed to obtain a simple and economical device, which already contained all the reagents necessary to perform the analysis. Moreover, the origami approach (i.e., folding the device in a suitable configuration during the analytical procedure) provided additional flow control in order to avoid any premature contact between the reactants. A commercial 3D printer was used to produce additional components (a device holder and a miniaturized dark box) for performing the chemiluminescence measurement by a portable CCD camera.
The device proved suitable for the measurement of glucose with a limit of detection of about 10 μM and a linear response up to 250 μM, and the total analysis time was 20 minutes. It was therefore adequate for measurement of glucose blood levels, even after a significant sample dilution to eliminate any possible matrix effect (physiological glucose blood levels range between 4.0 and 5.5 mM). To perform the analysis without the preliminary generation of a calibration curve, a device in which a glucose standard was analysed together with the sample was also developed.
In perspective, the field of application of this device could be much broader since it can be easily modified to measure by oxidase-catalyzed reactions other clinically relevant analytes (e.g., uric acid and lactic acid). Moreover, use of alternative light detectors, such as silicon diodes or CMOS cameras integrated into smartphones and tablets, is under investigation.

A NEW SENSITIVE CHEMILUMINESCENT ASSAY TO QUANTIFY INTRACELLULAR XANTHINE OXIDASE ACTIVITY IN LIVING ENDOTHELIAL CELLS

D. Calabria, C. Caliceti, A. Roda
Dipartimento di Chimica "Giacomo Ciamician", Alma Mater Studiorum-Università di Bologna, Bologna, Italia

Xanthine oxidase (XO), a key enzyme expressed in the vasculature of endothelial cells, catalyses the conversion of xanthine to uric acid. Excessive production of uric acid results in hyperuricemia linked to gout and cardiovascular diseases (CVD). Testing inhibition of XO is important for the screening of drugs or natural products potentially used to treat CVD. Several methods to evaluate XO activity have been reported but most of them are based on cell-free systems [1] or lysed cells and therefore poor predictive to human pathologies. In the present study, for the first time an *in vitro* chemiluminescent (CL) bioassay was developed to determine XO activity in living endothelial cells allowing to calculate the IC50 value of oxypurinol, the active metabolite of the conventional inhibitor drug allopurinol. The method is based on the measurement of intracellular CL emission of luminol in presence of XO-produced H_2O_2 with Fe^{2+}-EDTA complex as catalyst. Intracellular XO activity was measured in less than 20 minutes by the luminol/catalyst-based CL system obtaining [$(6\pm1)*10^{-7}$ mU/ml cell] with a detection limit of 0.4 μU/mL and quantification limit of 1.3 μU/mL. Oxypurinol addition (ranging from 0.5 to 5.0 μM) caused a linear decrease in luminol-based CL intensity, with an IC50 of 1.0±0.5 μM. Next, to demonstrate the applicability of the CL cell-based assay for intracellular XO inhibition on real samples, endothelial cells were treated with extracts of two fungi, *Ganoderma Lucidum* and *Cordyceps Sinensis*, to which are attributed several therapeutic properties (from anti-cancer activity to CVD prevention). In literature, the data relating to the chemical and pharmacological behaviour of these two fungi are few and in any case, have been carried out with old and outdated analytical methods. Once verified that the two families of fungi are not able to interfere with the CL detection reaction, their inhibition effects on XO activity were evaluated in cells obtaining an IC50 of 28 ± 4 μg/ml and of 14 ± 3 μg/ml for *Ganoderma Lucidum* and *Cordyceps Sinesis*, respectively. The CL developed method is low-cost, rapid, reproducible and could be used on small quantities of whole cells (3.500 cells) resulting in a more representative and predictive bioassay to study XO inhibitors *in vitro*.

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FLOW FIELD-FLOW FRACTIONATION BASED APPROACH AS ANALYTICAL TOOL FOR NANOMATERIAL SELECTION AND APPLICATION IN HEALTHCARE

V. Marassi[a], L. Di Cristo[b], B. Roda[a], A. Zattoni[a], S. Casolari[a], A.L. Costa[c], A. Prina-Mello[b], P. Reschiglian[a]
[a] Department of Chemistry "G. Ciamician", Via Selmi 2, 40126 Bologna, Italy
[b] Department of Clinical Medicine, Trinity Translational Medicine Institute (TTMI), School of Medicine, Trinity College Dublin, Dublin 8, Ireland
[c] ISTEC-CNR, Via Granarolo, 40126 Faenza, Italy

In a world where silver nanoparticles (AgNPs) are more and more employed in various aspects of life, either as part of textiles , or as drug carriers , additives or medical devices , it is important to determine their properties and to understand to what extent –and in which way- such materials in the nanoscale form interact with living organisms and the environment. The access to suitable analytical tools for characterisation is of primary importance. The assessment cannot be limited to an accurate description of the newly composed material, but needs to be equally reliable when considering the modified state of AgNPs, which undergo changes in composition, size, shape and core-shell properties when in the exposure medium (biological testing or environment).[1] These modifications in fact influence the overall toxicity of engineered nanoparticles and can cause adverse effects upon exposure.[2]
Currently employed characterization techniques like transmission electron microscopy (TEM) and dynamic light scattering (DLS) present various limitations: batch analyses in DLS cannot provide information about the shape of the particles but only their hydrodynamic radius, while TEM analyses requires manipulation (drying) of the sample and is not representative of a suspension. The introduction of an in-flow separation technique as a characterisation step can both provide reliable data regarding samples in suspension and provide collectable fractions to be individually characterised/tested.
The aim of this work is to analytically distinguish among the colloidal properties of differently coated silver nanoparticles (AgNPs) when dispersed in aqueous media. In this study we will present a dataset based on their physicochemical properties, in order to provide the selection criteria for ranking the best performing material for healthcare applications.
By exploiting the coupling of a soft separation technique (hollow fiber flow field flow fractionation, HF5) with various detectors online and offline, we determined size, shape, surface charge and ionic release of the particles at the native state.

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HOST-GUEST COMPLEXES BETWEEN CYCLODEXTRIN DERIVATIVES AND DULOXETINE: ENANTIOSEPARATION STUDY IN CE AND IN VIVO DRUG DURATION OF ACTION

M. Seggio[1], S. Chiechio[2], G. Pappalardo[3], A. Giuffrida[1]
[1]Dipartiment of Chemical Sciences, University of Catania, Viale Andrea Doria, 6 – 95125 Catania, Italy;
[2]Department of Drug Sciences, University of Catania, Viale Andrea Doria, 6 – 95125 Catania, Italy;
[3]National Research Council-Institute of Biostructure and Bioimaging, Via Paolo Gaifami ,18–95126 Catania, Italy

The role of cyclodextrins in drug delivery has advanced in recent years and this may be attributed to its biocompatibility and well established synthesis. Chemical modification of CDs has shown to extend the physicochemical properties and the host ability for a variety of drugs. β-CDs have been widely used in the early stages of pharmaceutical applications due to its ready availability and its cavity size suitability for a wide range of drugs.
Cyclodextrin (CD) assisted capillary electrophoresis (CE) has shown to be a powerful tool to carry out chiral separations since it allows short analysis times, high separation efficiency, versatility and feasibility to incorporate a great variety of chiral selectors to obtain high resolutions.
Herein we spectrophotometrically studied the host-guest complexes obtained between different β-CD derivatives and duloxetine: an antidepressant that belongs to SNRI class. It showed an analgesic activity and it was approved for the treatment of certain forms of chronic pain [1]. Thus, the ability of succinyl-β-CD to form complexes with duloxetine racemate was used in CE [2] and the enantiomeric resolution by electrokinetic chromatography (CD-EKC) was obtained.
Furthermore, the behavioural studies in vivo showed a change on the analgesic activity of duloxetine. The result of dosage of the complex 1:1 duloxetine : succinyl-β-CD, compared to the free drug dosage, was an increase of the duration of action.

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DETERMINATION OF ALDOSTERONE, CORTISOL, AND 8-ISO-$PGF_{2\alpha}$ IN ORAL FLUID SAMPLES BY UHPLC-MS/MS

F.G. Bellagambi[1], S. Ghimenti[1], T. Lomonaco[1], D. Biagini[1], F. Di Francesco[1], M.G. Trivella[1], M. Marzilli[2], R. Fuoco[1]
[1]Dipartimento di Chimica, Università di Pisa, Via Giuseppe Moruzzi, 13 – 56124 Pisa
[2] Dipartimento di Patologia Chirurgica, Medica, Molecolare e dell'Area Critica, Università di Pisa, Via Savi, 10 – 56126 Pisa

Aldosterone is an endogenous mineral corticosteroid whose primary physiological function is to regulate both the metabolism of sodium and potassium ions, and the volume of extracellular fluid and blood pressure. Similarly, cortisol is known to unfavorably affect classic cardiovascular risk factors such as hypertension and insulin resistance. Isoprostanes such as 8-iso-$PGF_{2\alpha}$ are a unique series of prostaglandin-like compounds and reliable markers of lipid peroxidation. Due to their role in the pathogenetic mechanism, and since their levels in oral fluid are correlated with the free amounts in blood, the non-invasive measurement of aldosterone, cortisol and 8-iso-$PGF_{2\alpha}$ in oral fluid may be a useful tool for monitoring patients affected by heart failure.
In this work, the development and validation of an analytical procedure for the determination of aldosterone, cortisol and 8-iso-$PGF_{2\alpha}$ by UHPLC-MS/MS in a single chromatographic run is described. An optimized liquid-liquid extraction procedure and the influence of sampling parameters such as oral fluid flow rate and pH on the concentrations of analytes are also presented.

Acknowledgement. This work was supported by the project PHC-643694 HEARTEN, funded by the European Commission under the H2020 programme.

STUDY OF THE FORMATION OF BINARY AND TERNARY COMPLEXES OF ADRENALINE WITH DIFFERENT CATIONS OF BIOLOGICAL AND ENVIRONMENTAL INTEREST IN NaCl AQUEOUS SOLUTION AT DIFFERENT IONIC STRENGTHS

R.M. Cigala, F. Crea, C. Foti, F. Giacobello, D. Milea
Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università degli Studi di Messina, Viale F. Stagno d'Alcontres, 31 – 98166 Messina

Our group has been involved during the last years in studies aimed at the determination of the thermodynamic aqueous parameters of different classes of organic ligands of biological and pharmaceutical interest. The knowledge of these parameters is a very important property for pharmaceutical product design, and they influence the pharmacokinetics, such as the release, transport and the degree of absorption in the organism.
Data regarding the thermodynamic aqueous properties of adrenaline appear till now few and quite confusing, and no systematic modeling study regarding their dependence on the experimental conditions (ionic medium, ionic strength and temperature) is reported.
The main aim of our investigation is to give an important contribution on the knowledge of the thermodynamic aqueous properties and sequestering ability of such ligand towards some metal (UO_2^{2+}; Cu^{2+}; CH_3Hg^{+}) ions of biological and environmental interest in NaCl aqueous solutions at different ionic strengths.
In order to give a further contribution to the speciation studies of this ligand, the formation of mixed metal (UO_2^{2+}/Cu^{2+}) species with adrenaline were investigated at I = 0.15 mol L^{-1}; similar investigation was also carried out checking the possible formation of mixed ligand species Cu^{2+}/adrenaline-histamine in the same condition. Calorimetric measurements were carried out at I = 0.5 mol L^{-1} in order to determine the enthalpy and entropy change values involved in the formation of the species.
The different speciation schemes were compared between them and the sequestering ability was estimate by means of the $pL_{0.5}$ parameter.
The dependence of such thermodynamic parameters on the ionic strength was modeled by means of an extended Debye-Huckel equation and of the SIT (Specific ion Interaction Theory) approach.
The sparingly soluble species obtained during the potentiometric titrations were studied and characterized by means of the TGA-FTIR analysis.

DIRECT QUANTITATIVE ANALYSIS OF SPECTROSCOPIC DATA BY CHEMOMETRICS AND SHRINKAGE METHODS

D. Melucci[1], A. Zappi[1], F. De Laurentiis[1], E. Brattich[1], L. Tositti[1]
[1]Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via Francesco Selmi, 2 – 40126 Bologna

Non-destructive methods are highly desirable in chemical analysis because they allow to investigate samples without alterations nor biases, additionally allowing to minimize analysis time and costs and preserve samples for further analysis.
Among the analytical methods available for sample characterization, many spectroscopic techniques are presently available; they are currently widely used due to their high performance in terms of chemical information, low cost, easy sampling preparation and widespread availability. This is especially true for infrared-techniques, Raman spectroscopy or X-ray diffraction. In most cases, all of these techniques are typically used on a qualitative basis owing to the complexity of signals generated both by multiple interactions as well as by compositional complexity. These effects have often been so far insoluble using a traditional approach. In fact, for qualitative investigation many analytical procedures are available, mainly based on spectroscopic characterization. However, the quantitative approach is still an open issue, because the matrix effect might be really hard to solve and hinders the creation of univariate calibration methods in interpolation mode.
Chemometrics offer both an improvement of qualitative methods and a possible solution for still unsolved quantitative problems. The multivariate standard addition calibration based on Partial Least Square Regression (PLSR) combined with Net Analyte Signal (NAS) calculation allows to bypass the matrix effect. Further step may be the introduction of shrinkage methods as Least Absolute Shrinkage and Selection Operator (LASSO), Elastic Net or Sparse Partial Least Square (SPLS) regression in order to select the most relevant variables and clean the signal from analytical noise.
In this work we present some examples of successful application of state-of-the-art chemometric methodologies to the quantitative analysis of samples subjected to Raman and FT-IR/ATR spectroscopy.
The cases described concerns

a) The application of PLSR, shrinkage methods and NAS to the analysis of biogenic silica (opal) in Antarctic marine sediments
b) The application of SPLS and NAS to Raman signal of paraffin in a beeswax matrix.

USE OF MULTIVARIATE IMAGE ANALYSIS FOR THE EVALUATION OF GRAPE RIPENING

G. Orlandi[1], R. Calvini[1], G. Foca[1], A. Ulrici[1], G. Vasile Simone[2], L. Pigani[2]
[1]Dipartimento di Scienze della Vita, Università di Modena e Reggio Emilia, Via Amendola 2, 42122 Reggio Emilia, Italia
[2]Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via Campi 183, 41125 Modena, Italia

In viticulture, the change in colour of grapes is an important attribute to define the ripening, which significantly influences the quality of wine.
In this context, the aim of the present study is to investigate the use of digital images for a fast and cheap monitoring of the degree of grape ripening.
For this purpose, 3 different grape varieties were considered: Ancellotta, Malbo Gentile and Lambrusco Marani. For each variety, 100 g grape samples were collected during 5 subsequent harvest times at 2 week intervals. Each grape sample was pressed and, after maceration, 8 aliquots of 50 µl of the extract were deposited on a white sheet of absorbent paper. Then, RGB images of the papers were acquired using a common flatbed scanner.
Each RGB image was converted into a one-dimensional signal, named *colourgram*, which codifies the colour properties of the image. In particular, the colourgrams approach is based on an algorithm that calculates the frequency distribution curves of a series of colour related parameters and then merges them in sequence to give a 4900 points-long signal [1].
The dataset of colourgrams was analyzed using proper chemometric techniques, in order to extract the information useful to determine the level of grape ripening of the corresponding grape samples. To this aim, Principal Component Analysis (PCA) was calculated on the colourgrams matrix for a prior explorative analysis showing that, for each considered variety, the samples were partially distributed along PC1 according to the harvest time.
Finally, calibration models were developed using Partial Least Squares (PLS) and interval-Partial Least Squares (iPLS) regression methods, in order to define the correlation between the images and a series of parameters that are generally extracted from the UV-vis spectra of the must samples, like e.g., the total polyphenols content, the colour index, the amount of anthocyanins and flavonoids [2].

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DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN LICHENS, BIOMONITORS OF AIR POLLUTION

M. Casale[1], P. Giordani[1], P. Malaspina[2], M. Di Carro[3], V. Sciascia[3], C. Mirasole[3], E. Magi[3].
[1]Dipartimento di Farmacia, Università degli Studi di Genova, Viale Cembrano 4 – 16148 Genova
[2]Dipartimento di Scienze della Terra dell'Ambiente e della Vita, Università degli Studi di Genova, Corso Europa 26 - 16126 Genova
[3]Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, - 16146 Genova

Polycyclic aromatic hydrocarbons (PAHs) are hydrocarbons that are composed of multiple aromatic rings (organic rings in which the electrons are delocalized). PAHs have been identified as carcinogenic and mutagenic, as well as teratogenic [1].
Recent studies demonstrated that lichens may be considered suitable biomonitors for the assessment of PAHs in the atmosphere. Lichens are symbiotic associations between a fungus and a photosynthetic partner(s).
In this study, a fast, simple and 'green' approach, based on spectrofluorimetry and chemometrics, for the determination of polycyclic aromatic hydrocarbons (PAHs) in lichens used as biomonitors of air pollution is presented.
Lichen thalli of Pseudevernia furfuracea, collected far from local sources of air pollution, have been exposed to the air for three months in different areas in the Liguria region. The transplanted thalli, retrieved at the end of the exposure period of 3 months, have been analyzed by spectrofluorimetry and also by GC/MS as a reference method.
The possibility to predict the quantity of PAHs in the lichen thalli was investigated comparing the spectra with the GC/MS determination.
Moreover, a comparison with the values of environmental pollutants recorded during the exposure period of lichens by the Regional Agency for Environmental Protection was made, with the final objective of relating PAH values in lichens with their atmospheric concentrations.

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A MULTIVARIATE STRATEGY FOR THE ENHANCEMENT OF SPATIAL RESOLUTION IN HYPERSPECTRAL MAPS

P. Oliveri[1], G. Sciutto[2], E. Catelli[3], S. Prati[2], R. Mazzeo[2], R. Leardi[1]
[1]Department of Pharmacy, Univ. of Genoa, Via Brigata Salerno, 13 – 16147, Italy
[2]Microchemistry and Microscopy Art Diagnostic Laboratory, Univ. of Bologna, Via Guaccimanni, 42 – 48121, Italy
[3]Department of Chemistry, Norwegian Univ. of Science and Technology, Høgskoleringen 5, Realfagbygget, Norway

The present work was focused on the evaluation of a multivariate strategy for enhancing the spatial resolution of hyperspectral maps acquired on painted surfaces by different spectroscopic point-scan systems (XRF, FT-MIR and Raman microscopy). To this aim, hyperspectral maps were processed together with multichannel images – acquired, on the same surface area, at a spatial resolution that is typically 8~10 times higher – following a peculiar mid-level data fusion strategy. Thus, the fusion/resolution enhancement procedure exploits the correlation between the two data blocks, as follows. 1) As the first step, PCA is performed separately on the two blocks, obtaining two sets of score maps, respectively. 2) The spatial resolution of the multichannel score image is reduced (by means of an averaging filter) to match that of the hyperspectral score map. 3) A PLS regression model is built, using the score map obtained from the spatially-reduced multichannel image as the X block, and the score map obtained from the hyperspectral cube as the Y block. Such a model is applied to predict the PC-score value of each pixel of the full-resolution multichannel PC-score map. The result is a hyperspectral score map at an enhanced resolution. Overfitting of PLS model is evidently implicated, since training and prediction datasets are strictly related. However, this does not represent a critical issue, since each PLS model is applied to a specific map and a general applicability is not required. The method was successfully applied on the study of painting samples to support a comprehensive interpretation of data. In particular, obtaining the same spatial resolution for maps acquired by different techniques on the same sample allows data fusion to be performed and, therefore, a more exhaustive characterisation of artistic materials to be achieved.

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APPLICATION OF XRF SPECTROSCOPY AND CHEMOMETRICS TO STUDY ARTISTIC PIGMENTS AND THEIR MIXTURES ONTO DIFFERENT SURFACES

P. Oliveri[1], N. Giovelli[2], A. Demelas[2], E. Parodi[2], R. Marazza[2], G. Petrillo[2]
[1]Department of Pharmacy, University of Genova, Via Brigata Salerno, 13 – 16147 Genova
[2]Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso, 31 – 16146 Genova

Availability of non-destructive, portable, straightforward, rapid and efficient analytical systems represents a key issue in chemical diagnosis of artistic specimens, for attribution, conservation and restoration purposes, supporting proper interventions on precious heritage materials.
In the present study, a portable X-ray fluorescence (XRF) spectrometer (Delta Standard 2000 Innov-X, Olympus Corporation) was used for the characterisation of pigments of artistic interest, by the "3-beam soil" acquisition mode (40 kV, 40 kV and 10 kV).
The whole XRF spectral profiles, regarded as fingerprints of samples under investigation, were submitted to multivariate pattern recognition by means of principal component analysis (PCA).
An in-house spectral database was developed recording XRF spectra of pure pigments applied onto a Plexiglas® support, which did not interfere under the experimental conditions.
Afterwards, pigments were analysed on real supports, typically encountered in ancient artworks in Liguria, such as slate stone and metals (mainly copper). Binary and ternary mixtures of the same pigments were also applied on the real supports and analysed.
PCA applied to spectral profiles was able to efficiently characterise pigments and their mixtures on the stone and metal supports, thanks to a comparison to the spectral database. Correlation coefficients between spectra were also considered. A detailed analysis of loading values allowed to characterise the elemental composition of each pigment.

A NEW CONCEPT OF HIGHER-ORDER SIMILARITY AND THE ROLE OF DISTANCE/SIMILARITY MEASURES IN LOCAL CLASSIFICATION METHODS

R. Todeschini, D. Ballabio, V. Consonni, F. Grisoni
Milano Chemometrics and QSAR Research Group, Department of Earth and Environmental Sciences, University of Milano-Bicocca, P.zza della Scienza, 1 – 20126 Milan (Italy)

This work introduces a new concept of similarity aiming to detect higher-order similarities between objects, from which meta-distances and meta-similarities are derived. A total of 100 meta-distances were obtained from a set of ten classical distances and were compared, in terms of classification performances, against classical distance measures. Classification methods based on local similarity analysis and several benchmark datasets were used. In several cases, the non-error rate (*NER*) of classifiers based on the new meta-distances was significantly higher than that of obtained using the classical Euclidean distance.

CLASSIFICATION PARAMETERS: AN EXTENDED MULTIVARIATE COMPARISON.

D. Ballabio, F. Grisoni, V. Consonni, R. Todeschini
Milano Chemometrics and QSAR Research Group, Department of Earth and Environmental Sciences, University of Milano-Bicocca, P.zza della Scienza, 1 – 20126 Milan (Italy)

This study targets the multivariate comparison of 19 well-established classification parameters. To this end, 32 benchmark datasets with different numbers of classes and different proportions of objects in each class were used. Principal Component Analysis was performed separately on the 2-class datasets and on multi-class datasets, and the relationships between the different classification parameters were critically discussed. Some optimal parameters for objectively assessing the classification performance of models were identified.

ARTIFICIAL NEURAL NETWORK OPTIMISATION OF UHPLC SEPARATION OF SAFFRON METABOLITES

A.A. D'Archivio[1], F. Di Donato[1], M. A. Maggi[2], F. Ruggieri[1]
[1]Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila, Via Vetoio, 67010 Coppito, L'Aquila, Italy
[2]Hortus Novus, Via Collepietro, 67100 L'Aquila, Italy

The main water-soluble ingredients of saffron, the dried stigma of *Crocus sativus* L. worldwide used as flavouring and colouring food additive, are crocetin esters, safranal, picrocrocin and its derivatives and flavonoids. High-performance liquid chromatography coupled to both diode array (DAD) and mass spectrometry (MS) detection has been widely applied in the analysis of polar saffron constituents. The aim of the present investigation is the optimisation of an UHPLC method, rarely used before in saffron characterisation, to improve knowledge on the metabolic profile of this precious spice. With this purpose, the combined effect of both eluent flux and gradient slope and column temperature on the chromatogram resolution has been investigated by response surface methodology (RSM). A three-level full factorial experimental design was adopted to plan the experiments. A feed-forward three-layer artificial network (ANN) was trained to model the resolutions of adjacent peaks in the chromatogram.

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A CHEMOMETRIC APPROACH: QUALITY ASSESSMENT FOR FOODSTUFFS USING HIGH-DATA FUSION METHODS

M. Coppolino[a], M. Gandolfi[a], D. Ballabio[a], V. Consonni[a], R. Todeschini[a], E. Robotti[b], E. Marengo[b], F. Gosetti[b], M. Manfredi[b]
[a]Milano Chemometrics and QSAR Research Group, Department of Earth and Environmental Sciences, University of Milano-Bicocca, P.zza della Scienza, 1 – 20126 Milan (Italy)
[b]Università del Piemonte Orientale "Amedeo Avogadro", Department of Science and Technological Innovation, V.le Teresa Michel, 11 - 15121 Alessandria

The consumers' interest in safe and DOP products and in the authenticity/quality of food commodities has been increasing in the last few years. Fraudulent acts, such as the use of cheaper ingredients in foodstuffs production, have become more and more relevant, so that the food quality assessment through analytical techniques is a fundamental step. The complexity of foodstuffs matrices makes each analytical technique susceptible to factors difficult to control. Because of this uncertainty, a multivariate approach to heuristically consider each analytical result can handle the problem and detect key production parameters for DOP's product qualities, provenience and authenticity. This study aims to improve the quality assessment (provenience, authenticity) of different food matrices (honey, Grana Padano, balsamic vinegar) by combining different sources of analytical information, such as NIR, IR, RAMAN spectroscopy, PTR-MS, TXRF spectrometry, chromatography through high-data fusion methods. The models obtained with different classification approaches, e.g. PCA-forward Linear Discriminant Analysis (LDA) and Partial-Least Squares Discriminant Analysis (PLSDA) were merged using advanced high-level data-fusion strategies, such as: Consensus, Bayes qualitative approach and Dempster-Shafer theory of evidence.

MULTIVARIATE PROCESS MONITORING APPLIED TO A MUNICIPAL SOLID WASTE (MSW) PLANT.

L. Favarato[1], G. Musetti[2], T. Brizzi[2], M. Cocchi[1]
[1]Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via Campi 103 – 41125 Modena
[2] CIS-MSW incineration plant of Ladurner Srl

After the entry into force of the European Directive on waste landfilling (EC, 1999) incineration with energy recovery became common practice in some European countries as the final disposal for the huge amounts of unsorted domestic waste daily generated. Waste-to-energy (WTE) conversion has also been the unsorted municipal solid waste (MSW) final disposal in countries with severe availability constraints on land resources.
Moreover, the increasingly competitive global market and the compliance with the very strict emissions limits imposed by legislation require higher energy efficiencies and lower emissions in the environment for the WTE incinerators operation.
In the era toward higher levels of automation, monitoring systems have been widely used to supervise complex process like municipal solid waste (MSW) incineration plant. Through a vast amount of data nets, monitoring system catches the real-time operating states of combustion system, air pollution treatment processes, and power generation process.
However, most of this data remain unused and still the univariate control charts approach is mainly adopted. Aim of this work is to apply Multivariate Statistical Process Monitoring starting from analysis of historical data by analyzing process data of a suitable working period of the plant. PCA of historical process data set allow capturing process variables correlation structure identifying time trends and highlighting troublesome periods as well as reference operative condition on which to implement multivariate control charts. Final objective is to build a monitoring system to detect fault and to make a diagnosis, in order to improve the safety and continuity of production.

CHEMOMETRICS IN FOOD AUTHENTICATION

M. Cocchi[1] , M. Li Vigni[1,2], C. Durante[2]

[1]Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via Campi 103 – 41125 Modena
[2] ChemSTAMP Srl, Via Campii 103 – 41125 Modena

According to ISO definition “an entity is authentic if it is what it claims to be.” and “Authentication is a process that is used to confirm that a claimed characteristic of an entity is actually correct”. When applied to food context this is actually a very broad concept covering several aspects including both the characterization and recognition of the identifiable features of a product as well as its accountability, in other words the degree of trustiness consumers associate to it. In practice, to assess authenticity it has to be taken into consideration in an integrated manner the several characteristics deliberately produced (sophistication, adulteration, counterfeit, appearance, etc.) or not (purity, contamination, degradation, etc.), but also the subjective consumer's perception of the worth of the product and issues such as terroir, authenticity, origin, production practice, etc. In this framework, quality control and authentication assessment need to go further traditional chemical analysis, which focuses on single classes of constituents/properties, and adopting a fingerprinting approach, trough fast, non-destructive techniques. In this perspective, the role of chemometrics is becoming basilar to efficiently extract the relevant information and to derive authenticity models. Nowadays, chemometrics offers tailored tools that allow exploratory data analysis, graphical representation and validation of the models during all steps of data processing as well as efficient storage, retrieval and sharing of information.
In the present contribution, the focus will be on illustrating the chemometrics pipeline highlighting the main issues, critical points and the successfully strategies with application to geographical traceability and typicality assessment.

DATA FUSION STRATEGIES FOR ENHANCING CLASSIFICATION PERFORMANCE: A CASE STUDY ON CYTOCHROME P450

S.Nembri, F.Grisoni, V.Consonni, D.Ballabio, R.Todeschini
Milano Chemometrics and QSAR Research Group, Department of Earth and Environmental Sciences, University of Milano-Bicocca, P.zza della Scienza, 1 – 20126 Milan (Italy)

Cytochromes P450 (CYP) are the main actors in the oxidation of xenotibiotics and play a crucial role in the drug metabolism. A central challenge of the drug discovery process is the prediction of the CYP – Drug interaction. In this context, Quantitative Structure-Activity Relationship (QSAR) and chemometric strategies can give a relevant contribution.
This work aims to develop classification models able to classify a molecule as active or inactive towards two of the most important CYP isoforms involved in drug metabolism, i.e. CYP3A4 and CYP2C9, by exploiting data fusion strategies to maximize the classification performance. Several benchmark and recently proposed classification methods were considered in combination with Genetic Algorithms on more than 9,000 molecules. The structural information was described by 1,472 Dragon molecular descriptors divided into 18 sets encoding different types of chemical information, which were used as independent variables. Low- and high-level data fusion strategies of different nature were explored for their ability to improve the prediction performance of individual models obtained (a) on single descriptor sets and/or (b) with a single classification method.
The results show that data fusion strategies can be a useful tool to improve the classification performance and encourage their exploitation in the field of QSAR and chemometrics.

ALIZARIN RED S-BASED ELECTROCHEMICAL SENSORS FOR THE SIMULTANEOUS DETERMINATION OF Fe(III) AND Cu(II)

G. Alberti, M. Pesavento, A. Salvi, R. Biesuz
Dipartimento di Chimica, Università degli Studi di Pavia, Via Taramelli, 12 – 27100 Pavia

Recently, the simultaneous determination of two or more analytes with simple and low cost sensors is one of the research challenges in chemistry. Electroanalytical methods are versatile techniques that offer high sensitivity, accuracy, and precision as well as large linear and dynamic range, with relatively low cost instrumentation.
In this framework, we have tried to develop Alizarin Red S based voltammetric sensors for the simultaneous determination of Fe(III) and Cu(II). In particular a self assembled monolayer (SAM) on gold electrode (Au-ARS) and a glassy carbon modified electrode (GC-ARS) were tested.
The preparation of the SAM on the gold surface was optimized by an experimental design and it required an immersion of a clean Au electrode in a 10 mM cysteamine alcoholic solution for 24 h, followed by soaking of the electrode in 2 mM aqueous solution of Alizarin Red S for other 24 h.
On the other hand, the modification of the glassy carbon surface was faster: the electrode was directly immersed in 6 mM Alizarin Red S aqueous solution just for 10 minutes.
Preliminarily, the characterization of each electrode was performed assessing the successful modification of the surface; specifically capacitance, surface coverage and electron transfer rate were evaluated.
As first task, for both electrodes, a single cation calibration was undertaken aiming the determination of the LOD, LOQ and the linear and dynamic ranges. For this purpose, the multivariate regression PLS, (Partial Least Square Regression) was applied. Compared to the classical univariate approach, by PLS the entire voltammogram was employed for the analysis overcoming the problems of measuring high and/or area of broad and not well defined peaks. All the more reason, a multivariate regression becomes essential to develop calibration models for the simultaneous analysis of the two cations.
The validity of the PLS models for Fe(III) and Cu(II) was verified analysing synthetic solutions, containing different quantity of both cations, and real samples.

ALL-ELECTROCHEMICAL SYNTHESIS OF COMPOSITE MATERIALS PLATINUM NANOPARTICLES/POLYPYRROLE NANOWIRES FOR SENSING APPLICATIONS.

A. Caroli, E. Mazzotta, S. Rella, A. Turco, C.Malitesta
Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento,Via Monteroni, 1 – 73100 Lecce.

In the last two decades great attention has been devoted to the design of composite materials consisting of a mixture of noble metal nanoparticles and organic phases (e.g. carbon nanotubes, graphene and conductive polymers) that present remarkable potential applications as they combine distinct properties of individual components within a single matrix with enhanced or new properties, such as, mass transport, high active surface area and optical properties. These features make composite materials ideal candidates for applications in catalysis, separation, sorption, solar cells, supercapacitors and fuel cells[1]. Moreover, composite materials show an efficient electrocatalytic activity towards small organic molecules which can be exploited for the fabrication of sensing devices[2]. In the present study, a composite material consisting of polypyrrole nanowires (PPy-NWs) and platinum nanoparticles (PtNPs) has been prepared by an all-electrochemical approach. PPy-NWs are electropolymerized by a template-free method[3], and Pt-NPs are electrodeposited by exploiting Costant Potential (CP), Cyclic Voltammetry (CV) and Potential Step (PS) techniques. In particular, for each method, a systematic investigation of experimental conditions potentially influencing PtNPs size, distribution, morphology and electroactivity, has been performed. Electrochemical, morphological and chemical characterization of PPy-NWs/PtNPs samples has been carried out. Scanning Electron Microscope (SEM) has been used to investigate PtNP distribution, morphology and size. X-ray Photoelectron Spectroscopy (XPS) provided chemical state information about deposited platinum. CV experiments on PPy-NWs/PtNPs allowed to estimate the amount of deposited platinum and the electroactive area. Dopamine was tested as case study molecule to verify the electrocatalytic activity of the composite materials by Differential Pulse Voltammetry (DPV) gaining satisfactory results in electrochemical oxidation experiments.

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APPLICATION OF AN ELECTRO-ACTIVATED GCE TO ON-LINE MONITORING OF ACETAMINOPHEN PHOTO-DEGRADATION

E. Chiavazza[1], S. Berto[1], M. Marletti[1], A. Giacomino[2], M. Malandrino[1], C. Barolo[1,3], E. Prenesti[1], O. Abollino[1], D. Vione[1].
[1]Dipartimento di Chimica, Università di Torino, Via P. Giuria 7, 10125 Torino
[2]Dipartimento di Scienze e Tecnologia del Farmaco, Università di Torino, Via P. Giuria 9, 10125 Torino
[3]Centro INSTM e NIS, Università di Torino, Via Quarello 15A, 10135 Torino

This work is focused on the development of sensing devices for the determination of drugs in water samples and it is financed by the Fondazione Cassa Risparmio di Torino. The occurrence of pharmaceuticals in the environment is a problem of increasing concern, particularly for surface waters [1], where they can undergo chemical transformations due to abiotic processes such as photochemical reactions [2]. The acetaminophen (AP) is one of the most widely used pharmaceuticals [3]. AP is rather effectively degraded by biological processes, but appreciable concentrations can still be found at wastewater treatment plants effluents or in surface waters [4]. Several studies have investigated the fate of AP [5], determining a complex net of photochemical reactions. The monitoring of AP time trend under irradiation is usually carried out by HPLC and the degradation by-products are identified by high-resolution mass spectrometry. In this work, we start developing an electrochemical set-up for a fast real-time monitoring of the photochemical degradation of AP and the detection of its main photo-produced derivatives. This approach is based on a newly devised electro-activated glassy carbon electrode [6] that can detect AP at trace levels. The remarkable electrode sensitivity allows for the experiments to be carried out at AP concentrations that are closer to natural water conditions.

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ELECTROCHEMICAL ATOMIC LAYER DEPOSITION OF MOLYBDENUM CHALCOGENIDES

A. De Luca[1], A. Giaccherini[1], A. Comparini[1], S. Caporali[1], E. Piciollo[2] F. Di Benedetto[3], M. Innocenti[1]
[1] Dipartimento di Chimica, Università Degli Studi di Firenze, Firenze, Italy
[2] LEM galvanica, Italy
[3] Dipartimento di Scienze della Terra, Università Degli Studi di Firenze, Firenze, Italy

MoS_2 is an important IV–VI semiconductor, diamagnetic and with bandgap very close to silicon's (1.7 eV), thus fitting perfectly with solar emission. Moreover, 2-D structures of MoX_2 (X=S,Se) are considered very interesting materials for development of nanoelectronic devices.[1] The Electrochemical Atomic Layer Deposition (E-ALD) [2] is one of these techniques that allows us to produce thin films of semiconductor. E-ALD method was used to obtain semiconductor compounds in the form of thin films. The method is based on the alternate underpotential deposition of monolayer of the elements forming the compound. The UPD is a surface phenomenon that occurs when the deposition of one element precedes the massive electrodeposition. The UPD allows the perfect control of deposition of different kind of elements making possible to deposit highly defined nanostructures with a layer-by-layer control. The technical advantage is the possibility to modulate and to modify the parameters that influence the electrodeposition. That means that conditions for deposition can be adjusted concerning potential, pH, reactants and so on. UPD anodic electrodeposition of Na_2S on crystalline Ag[111] electrode is well-known, so the research move to discover the optimal conditions to depose Mo on Ag(111) and Ag(111)/X from a solution of MoO_4^{2-} in alkaline buffer. The UPD is a phenomenon limited by the surface of the electrode, so it's possible to change the time of the deposition to confirm that just a monolayer is involved in faradic process. Voltammetric techniques, such as anodic and cyclic voltammetry, suggest the occurring of a surface limited reaction leading to the deposition of Mo.

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COMBINED ELECTROCHEMICAL AND SPECTROSCOPIC APPROACH FOR TRACE LEAD ANALYSIS IN OLIVE OILS USING RTIL ELECTROLYTE

M. A. Baldo, A. M. Stortini, L. M. Moretto, P. Ugo
Università Ca' Foscari Venezia. Department of Molecular Sciences and Nanosystems. Via Torino 155 Mestre, Venezia (Italy)

Trace heavy metals dangerous to human health can be present not only in aqueous solutions, but also in non-aqueous matrices such as oil or fat. The analysis of metal ions in such highly viscous organic matrix by using conventional analytical procedures is rather challenging since it requires the application of series of delicate and time-consuming pretreatment steps which can be a source of contamination of the sample, possibly reflecting in scarce accuracy and precision.
In this work we present a novel analytical approach that combines electrochemical preconcentration with spectroscopic analysis, focusing on the determination of lead in oil as a case study. In order to perform electrochemical experiments in such a complex and low-conductive food matrix, the room temperature ionic liquid (RTIL) [P14,6,6,6]+[NTf2]-, which is soluble in vegetable oils, was used as supporting electrolyte [1,2]. For the development and validation of the analytical procedure, at first, standard solutions of lead in non-aqueous medium were generated by galvanostatic anodic dissolution of high-purity Pb in RTIL. By controlling the dissolution time, a set of Pb2+/[P14,6,6,6]+[NTf2]- standards with C = 10 ÷ 200 mg Kg-1, was prepared. Such a procedure was validated by AAS or ICP-MS analysis of the Pb2+ standards so produced, after careful mineralization in a microwave unit by a digestion protocol properly set up.
The final analytical strategy developed for the assessment of Pb content in oils include: mixing of the oil with the RTIL; potentiostatic electrochemical metal deposition from the tested oil sample; potentiostatic anodic stripping of the metal deposit after transfer to aqueous solution; spectroscopic (ICP-MS or GF-AAS) or voltammetric analysis of the solution collected.
The feasibility and performances of the analytical protocol were tested and validated in standard solutions of Pb2+ in RTIL, and in oil samples mixed with RTIL and spiked with Pb. The proposed procedure was finally applied to the determination of Pb content in some Italian olive oils.
The combination of a simple and fast electrochemical preconcentration/stripping protocol followed by spectroscopic analytical quantification represents a promising analytical strategy for the assessment of trace metal contamination in edible oils, avoiding mineralization or other time-consuming pretreatments of the complex food matrix.

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PAPER–BASED SENSORS FOR AMPEROMETRIC AND CONDUCTIMETRIC DETERMINATION OF CARBOHYDRATES AND AMINES

F. Terzi[1], S. Ruggeri[1], B. Zanfrognini[1], E. Corsi[1], N. Dossi[2], E. Piccin[3], G. M. Casagrande[3], R. Seeber[1]
[1]Dipartimento di Scienze Chimiche Geologiche, Università di Modena e Reggio Emilia, Via Campi, 103 – 41125 Modena
[2]Dipartimento di Scienze degli Alimenti, Università di Udine, Via Cotonificio 108 – 33100, Udine
[3]Department of Chemistry, Federal University of Minas Gerais – 31270-901, Belo Horizonte, Brazil

In the present contribution we describe the development of two electrode systems based on paper, modified by electrically conductive coatings. The systems deals with the problem related to food quality and safety, namely the estimation of the total carbohydrate concentration through amperometry and of ammonia and biogenic amines through conductimetry. The well known drawback of electrode fouling has been addressed using disposable sensors.
The determination of the total carbohydrate content both in raw materials and in final foodstuffs represents one of the most widespread analyses in food industry. To this aim a conductive ink based on Cu nanoparticles, graphite flakes, and an organic binder, namely polystyrene, dissolved in toluene, have been employed. As to sample pretreatment, only a simple dilution of the samples of carbohydrates in 1 M KOH is required. An experimental design has been employed in order to identify the most effective ink formulation and the quantities defining the DPV potential waveform. The effectiveness of the disposable electrodes has been tested in real matrices, namely, in soft drinks. The results in terms of accuracy in the estimation of the analyte concentration are satisfactory: on the basis of t-Student test, estimated and actual concentration values are well compatible with each other (ca. 10% maximum error).
As to amines, their determination in industrial settings is essential for safety reasons. To this aim gas phase conductimetric sensors have been fabricated using paper slabs modified with polypyrrole. The polymer has been deposited directly onto the surface of the paper fibres through chemical polymerisation by means of a $FeCl_3$ solution. A careful choice of the experimental conditions, such as the amount of pyrrole and $FeCl_3$ concentration, leads to the formation of homogeneous and reproducible films. Reproducible responses with respect to ammonia and different amines have been obtained through the use of custom made flow cell, fabricated using 3D printing. The interference due to water and other organic species such as alcohols or aromatic solvents resulted very limited.

VOLTAMMETRIC BEHAVIOR OF IRINOTECAN IN ACETONITRILE AT MACRO AND MICROELECTRODES AND ITS DETECTION AT SUB-MICROMOLAR LEVELS

G. Bonazza[1], S. Daniele[1], S. Tartaggia[2], F. Polo[2], G. Toffoli[2]
[1]Department of Molecular Science and Nanosystems, University Cà Foscari Venice, Via Torino 155, Mestre-Venice.
[2]National Cancer Institute (CRO), Via Franco Gallini 2, 33081, Aviano, Pordenone.

Irinotecan (CPT-11) is a pro-drug currently used in several cancer regimens, mainly Colorectal Cancer [1]. It is activated by the enzyme Liver-carboxylesterase to provide 7-ethyl-10-hydroxycamptothecin (SN-38), which is a potent topoisomerase I inhibitor. CPT-11, however, has a narrow therapeutic range. This involves a continuous monitoring of the drug amount in body fluids, and eventually varying the drug dose, to avoid side effects, such as neutropenia and diarrhea. Irinotecan pharmacokinetics and pharmacodynamics strictly depend on patients' genetic background, thus showing a quite wide interindividual variability. All this implies a therapeutic drug monitoring (TDM) of both pro-drug and its main metabolite SN-38 [1]. To these purpose analytical methodologies based on high performance liquid chromatography, mass spectrometry and spectrophotometry are employed. These techniques require expensive apparatuses and are time consuming, while rapid and inexpensive procedures would be desirable for these kinds of measurements. Electroanalytical methods are attractive candidates to overcome the above drawbacks, thanks to their low cost, short analysis time and high sensitivity.
In this paper we present an electroanalytical investigation for the detection of irinotecan at sub-micromolar levels using either macro- and micro-electrodes. The voltammetric behaviour of CPT-11 has been studied in acetonitrile media, using glassy carbon and platinum electrodes. Acetonitrile has been chosen as the solvent, as it is often employed as denaturing agent for biological samples (i.e. blood serum). Cyclic voltammograms displayed a quite complex mechanism in both cathodic and anodic scans, in which, however, processes located at about -0.95 and 1.25 *vs.* Ag (pseudo-reference electrode), respectively, have proven to be suitable for quantification. Calibration curves have been performed using cyclic voltammetry and differential pulse voltammetry. Relevant current responses against irinotecan concentration, under optimised conditions, provided linear responses over the range 8 $x10^{-7}$ - 1.1 x 10^{-5} M and a detection limit of 1.28 x 10^{-7} M.

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HYDROPHILIC NANOPARTICLES FROM CARBON BLACK OXIDATION: ACID-BASE CHARACTERIZATION

C.Manfredi[1], S.Volino[1], M.Alfé[2], V.Gargiulo[2], F.Di Natale[2]
[1]Dipartimento di Scienze Chimiche, Università degli Studi di Napoli, Via Cintia, 45 – 80126 Napoli
[2]Dipartimento di Ingegneria Chimica, dei Materiali, e della Produzione Industriale, Università degli Studi di Napoli Federico II, P.le Tecchio, 80 – 80125 Napoli

Carbon blacks (CB) are carbonaceous materials that have a low hydrogen content, high specific surface area, and a great structural variability on the mesoscopic scale, which is strongly dependent on the synthesis conditions.[1] CB are largely composed of hydrophobic material organised, at the nanoscale level, in graphene layers that have various degrees of deviation from planarity and a different amount of the less organised soot areas (i.e., amorphous and disordered carbons) that make CB particles more reactive than graphite.[2] CB oxidation methods in gas-phase (i.e., air, nitrogen oxide, and ozone) and liquid-phase (i.e., nitric acid, potassium permanganate, potassium dichromate)[3,4] are extensively used to improve the CB dispersibility in aqueous media. In this work we propose a study on the hydrophilic carbonaceous nanoparticles (HNPs) of uniform size with a very good degree of dispersion in water obtained through wet oxidation of CB with hot nitric acid. This process provided selective functionalization with oxygen functional groups such as carboxylics, at the edge of the graphitic layers[5,6] of the CB particles which makes possible the exploitation of heavy metal adsorption capability.
Acidity constants and site concentrations for the major surface functional group on the HNPs surface samples, obtained by varying the CB particle contact time with hot nitric acid, were determined by coulometric–potentiometric titrations. Zn(II) adsorption capacity tests by polarographic technique have been carried out.

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A THERMODYNAMIC STUDY ON THE RESVERATROL-WATER SYSTEM

C.Manfredi, C.Pepe, S.Volino, M.Annetta, M.Trifuoggi
Dipartimento di Scienze Chimiche, Università di Napoli, Via Cintia 46, 80126 Napoli, Italia

Research on the effects of dietary polyphenols on human health has developed considerably in the past. It strongly supports a role for polyphenols in the prevention of degenerative diseases, particularly cardiovascular diseases and cancers[1,2]. The antioxidant properties of polyphenols have been widely studied, but it has become clear that the mechanisms of action of polyphenols go beyond the modulation of oxidative stress. In nature we can find resveratrol as two diastereoisomers: (Z)- resveratrol and (E)- resveratrol that presents a major stability[3]

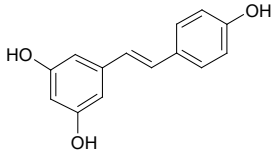

Fig1.- trans-resveratrolo

In the present work is presented a thermodynamic study on resveratrol in aqueous solutions. Acid-base properties of resveratrol have been investigated. The study has been conducted at 25.00 ± 0.02°C, in constant ionic medium, NaCl 0.5 M/ethanol 4% (v/v) by using potentiometry, UV-Vis spectrophotometry (absorption and emission), chromatography (HPLC). A chemical investigation on the interaction of the resveratrol with metals of biological interest, such as Mn^{2+} and Cu^{2+} has also been carried out. The study indicated the formation of a predominating Me(II)-resveratrol, mononuclear complexes.

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PHOTOACID SWITCHING IN FUSED-RING N-RICH AROMATICS

C.Manfredi[1], M.V.Ferrara[1], S.Volino[1], P.Scarano[1], C.Pepe[1], R.Centore[1], A.Peluso[2], A.Capobianco[2]

[1]Dipartimento di Scienze Chimiche, Università di Napoli, Via Cintia 46, 80126 Napoli, Italia
[2]Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, Via Giovanni Paolo II 132, Cap 84084, Fisciano (SA), Italia

[1,2,4]triazolo[3,2-c][1,2,4]triazole is a simple fused-ring N-rich aromatic system, with remarkable properties with respect to acid-base behavior and tautomerism[1-3]. Neutral heterobicycles (HL) exhibit amphoteric behaviour (they can deliver the N–H proton forming the conjugated base L^- and can accept up to two protons, forming the species H_2L^+ and H_3L^{++}) and show an unprecedented tautomeric switching upon protonation, as revealed by single crystal X-ray analysis and confirmed by theoretical calculations[4]. By varying the groups attached at the heterocycle, a remarkable shift of pKa$_i$ values, up to 5-6 units, is observed. The studies of the acid-base properties in the excited state show that the N-H group in neutral triazolo-triazoles has an intrinsic photobasic behavior. Singly protonated forms of the system have instead a photoacid behavior. If a photoacid phenol group is attached at position 7 of the intrinsically photobasic triazolo-triazole unit, the interaction between the two complementary photoactive functions in the same molecule is additive, in such a way that in the ground state N-H is more acid than O-H while the opposite holds in the excited state. So, between ground and excited state, the acid proton is delivered by different sites of the same molecule (photoacid switching).

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THERMODYNAMIC STUDY FOR THE PROTONATION OF HALLOYSITE

C. Bretti[1], S. Cataldo[2], A. Gianguzza[2], G. Lando[1], G. Lazzara[2], A. Pettignano[2], F. Siragusa[2], S. Sammartano[1]
[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Viale Ferdinando Stagno d'Alcontres 31 - 98166 Messina, Italy.
[2]Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze, Edificio 17 - 90128 Palermo, Italy

The Halloysite ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$) is an abundant and cheap clay and is considered one of the most promising nano structured and naturally occurring clay mineral. Large deposits of this material are present in France, Belgium, China, New Zealand and USA [1,2]. Among the spheroidal, tubular or platy morphologies, the tubular is the most common and abundant one. Typically, halloysite nanotubes (HNTs) are formed by 15 – 20 aluminosilicate layers, having a length of 1 ± 0.5 μm, and inner and outer diameters of 10 – 15 nm and 50 -70 nm, respectively [1]. In each layer, the SiOH and the AlOH groups are disposed on the external and the internal surfaces, respectively. As consequence, in each nanotube and in a large pH range, there is a charge separation between the inner and the outer surfaces. In particular, the inner surface is positively charged because of protonation of AlOH groups and the outer surface is negatively charged because of the gradual deprotonation of SiOH groups at pH higher than 2.
This charge separation is one of the most important features for the HNTs versatility and is strictly dependent on the acid – base properties of their functional groups. In this work, the protonation / deprotonation of SiOH and AlOH groups of HNTs is evaluated by ISE-H^+ potentiometric titrations of HNTs aqueous suspensions in different ionic media and ionic strengths ($0.025 \leq I$ / mol $L^{-1} \leq 0.750$) and in a wide pH range (2 – 11), at T = 25°C. ISE-H^+ potentiometric titration data have been processed by using the same models successfully used in a previous work for carboxylic and phenol groups of humic and fulvic substances [3]. Moreover, the change of superficial charge with the changing of pH was also evaluated by ζ potential measurements. Correlations between the ζ potential trend and the distribution of protonated and deprotonated species of HNTs were found.

1. Y.M. Lvov, D.G. Shchukin, H. Mohwald, R.R. Price, ACS Nano 2 (2008) 814-820.
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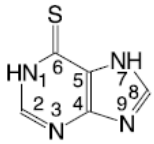
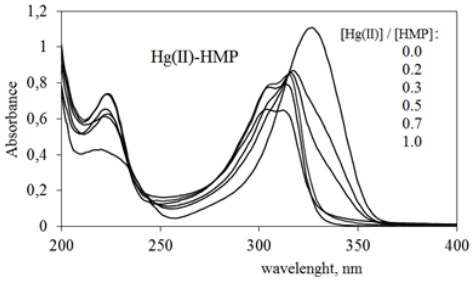
INTERACTION OF TOXIC METALS (Cd(II), Hg(II), Ni(II) AND Pb(II)) WITH 6-MERCAPTOPURINE IN METHANOL–SODIUM PERCHLORATE MEDIUM.

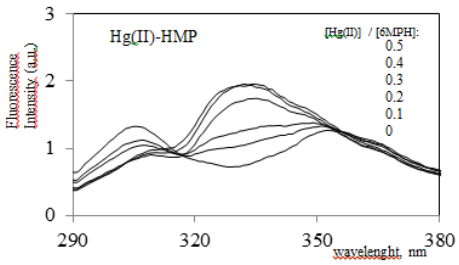
G. De Tommaso, M. Iuliano
Department of Chemical Sciences, University of Naples "Federico II" Via Cupa Nuova Cintia, 21– 80126 Naples (Italy).

Mercaptopurines exhibit a high activity against certain types of tumour [1]. HMP (1,7-dihydro-6*H*-purine-6-thione) is a purine derivative, containing double–bonded sulfur atom as a side group in the 6 position of the pyrimidinic ring, used for maintenance therapy of acute human leukemias. A spectrofluorimetric method for toxic metals detection (Hg, Cd, Ag and Pb) based in the reaction with HMP to form highly fluorescent complexes is described [2]. Interaction between Cd(II), Hg(II), Ni(II) e Pb(II) and HMP has been examined by potentiometric, UV-VIS spectrophotometric and spectrofluorimetric techniques. HMP is sparingly soluble in water (about 3×10^{-5} M) but soluble in methanol-water solutions. For this reason potentiometric studies have been conducted in methanol-0.1 M sodium perchlorate medium, by hydrogenionic concentration measurements with glass electrode.



Spectrophotometric Job's method has shown the composition of the complexes to be 1:1 and 1:2. Solution ^{1}H–NMR measurement and solid state FT–IR spectra indicate the coordination involves C(6)=S and N(7).





According to the Circular Dichroism and spectrofluorimetric studies DNA–binding affinity of toxic metal is reduced by HMP coordination.

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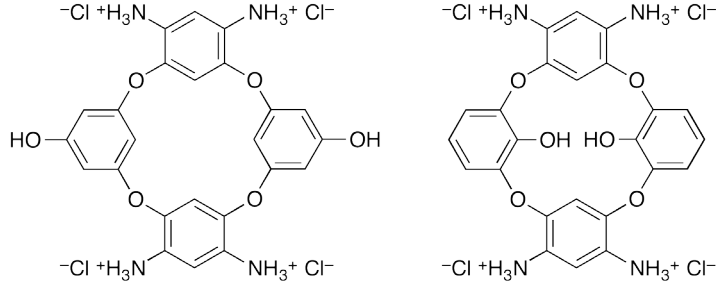
ACID BASE PROPERTIES OF WATER SOLUBLE OXACALIX[4]ARENES AND THERMODYNAMICS OF OMOCHARGED INTERACTION WITH PARAQUAT DICATION

C. Bretti, R.M. Cigala, G. Gattuso, A. Irto, G. Lando, N. Manganaro, S. Sammartano
Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli studi di Messina, Viale Ferdinando Stagno d'Alcontres, 31 – 98166 Messina (Italy)

The acid-base properties of two novel oxacalix[4]arene (see figure below) have been investigated by UV-vis spectroscopy in water and at different concentrations of aqueous NaCl solutions.



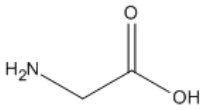
Data fitting with HypSpec revealed six displaceable protons, whose protonation constants values cover almost the entire pH range between 1.85 < pH < 10.75. The first four protonation constants belong to the amino groups, whereas the remaining two to the hydroxide groups, leading the molecules to have a net positive charge at pH < 6, and a negative charge at pH > 9. Small differences for the protonation constants of the two isomeric macrocycles depend on the different arrangement of the OH substituents, mirroring the behavior of the pyrogallol and phloroglucinol precursors. We have recently studied (by means of ^{1}H NMR titrations) the unusual omocharged interactions that are in action at low pH between the parent oxacalix[4]arene (i.e., without the hydroxide groups) and the paraquat dication [1],which are based on a delicate balance between electrostatic repulsion, Coulombic shielding by the chloride counterion and attractive π-stacking interactions. The macrocyles investigated herein have a greater solubility in water than the parent derivative and their interactions with the paraquat dication have been determined by NMR and calorimetric titrations also in basic pH ranges, shedding light on the supramolecular interactions responsible for this associative event.

[1] Manganaro N. Lando G., Gargiulli C., Pisagatti I., Notti A., Pappalardo S., Parisi M. F., Gattuso G. Unique binding behaviour of water-soluble polycationic oxacalix[4]arene tweezers towards the paraquat dication. Chem. Comm. (2015) 51, 12657-12660

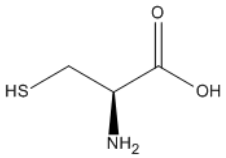
STUDY OF Al^{3+} INTERACTION WITH GLYCINE, CYSTEINE AND TRANEXAMIC ACID IN AQUEOUS SOLUTION

P. Cardiano, C. De Stefano, F. Giacobello, O. Giuffrè, S. Sammartano
Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali dell'Università degli Studi di Messina, Viale F. Stagno d'Alcontres, 31 – 98166 Messina

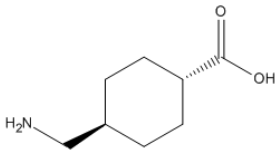
In the last decades, the extensive use of aluminium in many industrial fields, its natural distribution in the environment and the fact that it was recognized as the cause of several diseases, made it of large interest for speciation studies.[1,2]
This thermodynamic study focuses on the interaction between Al^{3+} and some ligands of biological interest, such as the amino acids glycine (**Gly**) and cysteine (**Cys**), and tranexamic acid (**Tranex**).



Gly



Cys



Tranex

Due to the formation of slightly soluble species some difficulties during experiments occurred, thus hindering the investigation above pH = 5. Speciation models in aqueous solution and thermodynamic formation parameters, by potentiometric and calorimetric titrations at t = 25 °C, I = 0.15 mol L^{-1} in NaCl aqueous solutions, were determined. Potentiometric titrations at I = 0.5 and 1 mol L^{-1} were also carried out. For all the systems, the formation of two or three species was observed, namely MLH, ML and $M_2L_2(OH)_2$ for **Gly**, ML, M_2L and MLOH for **Cys**, MLH and MLOH for **Tranex.** The stability of ML species is 7.18 and 11.91 for **Gly** and **Cys**, respectively at t = 25°C and I = 0.15 mol L^{-1}. The Al^{3+}-**Cys** speciation model and the formation constants of the most significant species were confirmed by spectrophotometric and ^{1}H-NMR measurements at t = 25°C and I = 0.15 mol L^{-1}. For all the systems the dependence of formation constants on ionic strength over the $0.1 \leq I$ / mol $L^{-1} \leq 1$ range was calculated. The sequestering ability of the three ligands under study towards Al^{3+}, through the $pL_{0.5}$ empirical parameter, was quantitatively evaluated.

[1] G. Crisponi, V. M. Nurchi, V. Bertolasi, M. Remelli, G. Faad, Coord. Chem. Rev. 256 (2012) 89-104.
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EXTRACTION OF HEAVY METALS IN DIFFERENT POLLUTED SOILS SAMPLES AND ANALYSIS BY ICP AND VOLTAMMETRIC TECHNIQUE.

C. Bretti[a)], G. Lando [a)], G. Yüce [b)], F. Italiano [c)] G. Sabatino [d)], S. Sammartano[a)]

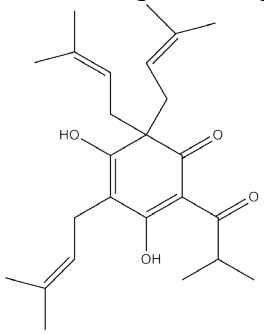
[a)]Dipartimento di Scienze Chimiche, Università degli Studi di Messina, Viale Ferdinando Stagno d'Alcontres, 31, I-98166 Messina (Vill. S. Agata), Italy. [b)]Hacettepe University Geological Engineering Department ANKARA Turkey. [c)] INGV - Via Ugo La Malfa, 153 - 90146 Palermo. [d)] Dipartimento di Fisica e Scienze della Terra, Università degli Studi di Messina, Viale Ferdinando Stagno d'Alcontres, 31, I-98166 Messina (Vill. S. Agata), Italy

In this contribution, the mineralogical, geochemical and chemical analysis of soil samples, coming from Hatay province (Turkey) are shown. The XRF analysis was performed to obtain information about the chemical composition in terms of major (Ca, Mg, Si, Fe, Al) and minor elements (heavy metals). The results evidenced the particular high values of Cr, Ni and Pb. Furthermore, XRPD analysis allowed to define the calcareous nature of soils, by the grain size point of view is a fine sand, that contain also an important zeolitic portion (Gismondine type like). Afterwards, the Afterwards, the soils underwent to washing procedures, using different extracting agents, mixing soils and solvent (1:10 ratio). The used extracting solutions consist of ultrapure water with addition of 0.01 M Na_2HPO_4 solution, 0.01 M EDTA and 0.01 M S, S-EDDS. pH, conductivity and concentration of Zn(II), Cu(II), Pb(II), Ni(II), Cr(III) and Cr(VI) were determined using potentiometry and voltammetry (hanging mercury drop electrode, HMDE). To determine the metal concentrations some procedures were opportunely proposed: i) the determination of Zn(II), Pb(II), and Cu(II) can be performed simultaneously in acidic media (pH ~ 2) with anodic stripping voltammetry and with 150s of deposition time, ii) Ni(II) must be determined, with cathodic stripping voltammetry and 90s of deposition time, using dimethylglioxime as complexing agent at high pH values, buffered at pH ~ 10.5 with NH_4OH/NH_4Cl, to avoid interferences of Zn(II) and iii) Cr(III) and Cr(IV) was determined in cathodic stripping voltammetry with low deposition time (0 to 10s) using saturated sodium DTPA as complexing agent, sodium nitrate (~ 0.6 M) as enhancer of the re-oxidation of Cr(II) to Cr(III) during the scan in 1 M ammonium formate buffered solution. In this last procedure, the control of the pH between 5.8 – 6.3 is fundamental. A sample pretreatment is necessary to avoid the interference of organic matter, for this reason the sample were filtered through a C-18 cartridge. In addition, for the separation of Cr(III) and Cr(VI), the C-18 filtered samples can be filtered again with a IC-H cartridge for the cationic exchange of Cr(III) with Na^+, allowing us to determine the speciation of Cr among its tri- and hexa-valent species. A validation procedure of the method was carried out.

ACID BASE PROPERTIES AND BINDING ABILITY OF HOPS EXTRACT: COLUPULONE

C. Bretti, R. M. Cigala, C. De Stefano, F. Giacobello, G. Lando, S. Sammartano
Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università degli Studi di Messina, Viale F. Stagno d'Alcontres, 31 – 98166 Messina

In the past, the Hops and its extracts were used in brewing as preservative and flavouring agent, now, its extracts are employed as source of phytoestrogenes and as an alternative to hormone replacement therapy. The Colupulone shows antibacterial properties and it is inhibitor for the tumor cell proliferation. From a chemical point of view, the Hops contains a mixture of three β-acids: lupulone, colupulone and adlupulone. In this study, a commercial extract was characterized by ^{1}H and ^{13}C-NMR, resulting that is mainly colupulone, (see figure) and the acid-base properties, the solubility and the complexing ability have been studied.
The solubility of the ligand determined in water (S =0.080 mmol·L^{-1}) and in different ionic media, (NaCl and KCl, where $S_{NaCl} > S_{KCl}$), at different salt concentrations, allowed us to calculate the Setschenow and the activity coefficients of the neutral species. Owing to the difficulty to dissolve suitable amount of Hops in water, the protonation constants were determined in a mixed water/methanol solution, to increase the solubility of the ligand. Two protonation steps were determined in $NaCl_{aq}$ and in KCl_{aq} at different ionic strengths ($0.1 \leq I$/mol L$^{-1} \leq 1.0$) and temperatures (T = 288.15, 298.15 and 318.15 K); the trend observed is that the logK^{H} in NaCl is higher than logK^{H} in KCl and in general the logK^{H} decreases increasing the temperature. The data obtained were fitted to model the ionic strength and temperature dependence, taking into account the percentage of methanol in the solution. The complexing ability of this ligand was tested towards some divalent metal cations, Ca^{2+}, Zn^{2+} and Sn^{2+}, by means different analytical techniques: potentiometry, voltammetry and UV-spectroscopy.



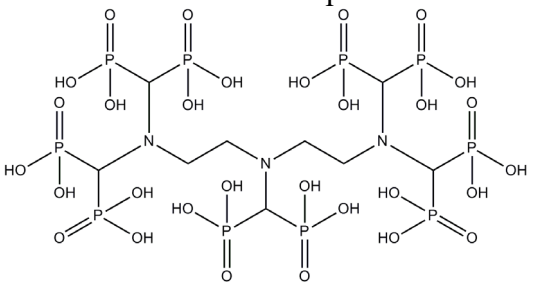
3,5-dihydroxy-2-isobutyryl-4,6,6-tris(3-methylbut-2-en-1-yl)cyclohexa-2,4-dienone

Colupulone

SEQUESTERING ABILITY OF DIETHYLENETRIAMINE-N,N,N',N'',N''-PENTAKIS-(METHYLENE PHOSPHONIC ACID) TOWARDS ALKYLTIN(IV) COMPOUNDS

P. Cardiano, C. Foti, O. Giuffrè, A. Irto, D. Milea
Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università degli Studi di Messina, Via Stagno d'Alcontres, 31 – 98166 Messina

In the last years, the use of classical chelanting agents like EDTA has been reduced in favour of new classes, which should be, possibly, more effective, selective, non-toxic, cheap and "eco compatible". In particular, the class of (poly)phosphonates looks very promising for the replacement of old ''complexones'' and, for some reasons, such as the high stability, the low toxicity; the coordinating ability of phosphonic derivatives toward several metal cations, they are widely used in many application fields, ranging from the industrial and technological to medicine. Among the most common phosphonates, diethylenetriamine-N,N,N',N'',N''-pentakis-(methylene phosphonic acid), *DTPMPA*, is becoming a preferred chelant in many applications in which strong metal chelation is desired, owing to the frequent absence of precipitation of some of its complexes over a wide pH range.



DTPMPA

In the light of the above considerations, we undertaken a systematic study DTPMP complexing ability towards alkyltin(IV) derivatives: the dialkyl $(CH_3)_2Sn^{2+}$ and $(C_2H_5)_2Sn^{2+}$, and the trialkyl $(CH_3)_3Sn^{+}$, $(C_2H_5)_3Sn^{+}$ and $(C_3H_7)_3Sn^{+}$ cations. Studies were performed by potentiometry in NaCl aqueous solution at $I = 0.1$ mol L^{-1} (for $(CH_3)_2Sn^{2+}$ also by varying the ionic strength in the range $0 < I \leq 1$ mol L^{-1}) and $T = 298.15$ K. In addition, for all systems, ^1H NMR investigations were carried out in order to confirm the potentiometric findings and to gain more information about the coordination. Finally, the sequestering power was quantified by the determination of $pL_{0.5}$ values (a semiempirical parameter which numerically represents the concentration of ligand able to sequester the 0.5 of metal fraction).

STIMULI-RESPONSIVE POLYMER-MODIFIED GRAPHENE OXIDE AS VERSATILE PLATFORM FOR (BIO)SENSING

C. Sgarlata[1], G. Consiglio[1], L. D'Urso[1], P. Di Pietro[1], G. Forte[2], G. Grasso[1], C. Satriano[1]
[1]Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale Andrea Doria 6, 95125, Catania, Italy
[2]Dipartimento di Scienze del Farmaco, Università degli Studi di Catania, Viale Andrea Doria 6, 95125, Catania, Italy

Stimuli-responsive materials have gained growing interest in a variety of fields including controlled drug delivery, tissue engineering as well as soft machines. Graphene oxide (GO) is a unique 2D nanocarbon material with extraordinary electronic, thermal and mechanical properties which exhibits oxygenated defects and thus provides a versatile platform for both covalent and non-covalent functionalization owing to its great surface activity and satisfactory solution processability.
In this work, GO substrates have been suitably functionalized to obtain multifunctional nanoplatforms in which the assembly states can be controlled by proper chemical stimuli for imaging and drug delivery applications [1]. In particular, the grafting of pH-responsive acrylate derivatives (PAA) [2] onto the surface of GO nanosheets has been optimized by monitoring the surface charge; the final product was fully characterized by spectroscopic (Raman, XPS, UV-vis and fluorescence), spectrometric (ToF-SIMS, ESI-MS) and microscopic (confocal microscopy, AFM, SEM) techniques both in solution and at the solid surface.
The response of such modified materials to different chemical stimuli (pH and ionic strength) was monitored by UV-vis and fluorescence experiments and further modeled by First Principle and MD calculations. The interactions of the GO-PAA samples with fluorescein-labeled human serum albumin (HSA) have been also investigated at different pH and ionic strength. Results obtained unveiled the promising features of these nanomaterials as sensing agents and helped to understand and control the processes occurring at the GO-(bio)molecule interface as well as the GO-(bio)molecule-target interactions in solution [3].

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[2] B. Wang, D. Yang, J. Z. Zhang, C. Xi, J. Hu, J. Phys. Chem. C 115 (2011) 24636–24641.
[3] This research was supported by the University of Catania (FIR 2014, 018B9A).

IDENTIFICATION OF GSR-OGSR IN DAILY FORENSIC CASEWORKS

M. A. Fabiano[1], R. Risoluti[1], A. Gregori[2], L. Ripani[2], S. Materazzi[1]
[1]Dipartimento di Chimica, "Sapienza" Università di Roma, P. le Aldo Moro 5, 00185 Roma
[2]Reparto Investigazioni Scientifiche RIS di Roma-Arma dei Carabinieri, Viale Tor di Quinto 151, 00191 Roma

Many criminal events are often associated with the use of firearms. It is ignored, in fact, the availability of weapons in Italy: the 10% of the population owns a gun or a rifle, data that are obtained from the only official database of the State Police that stores 1100000 weapons. From a forensic point of view, it is more and more required solutions for the legal character of the events to implement an accurate and probative scientific investigation.
The identification and the determination of the use of firearms played a fundamental role in crime scene investigation.
Gunshot residues (GSR) are substances which consists of unburnt and partially burnt particles that are derived from components of the cartridges, like primer and propellant, and that are formed as results of a shot. This type of residues may be of inorganic and organic nature (Inorganic Gunshot Residues-Organic Gunshot Residues).
This work aims at identifying alternative solutions to the critical issues of the current methods for the analysis of GSR-OGSR. These problems are related to the use of a new materials, based on "lead-free" or "nontoxic" ammunitions.
To overcome this problem, detecting organic components of GSR, i.e. the Organic Gun Shot Residues (OGSR), could be of help. To this end, different types of ammunitions were compared through SEM-EDX, for the analysis of GSR, and LC-MS, for the assessment of OGSR, and characterize the features particles of the ammunition used.
The preliminarly achieved results have shown that, combining informations from the analysis of GSR and OGSR, provide informations for investigative purposes, and confirm the hypothesis of crime, leading to a more accurate interpretation of the analytical results.

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ANALYSIS OF NEW PSYCHOACTIVE SUBSTANCES IN WHOLE BLOOD BY µ-SPE EXTRACTION AND LC-MS/MS DETECTION.

C. Montesano[1], G. Vannutelli[1], V. Piccirilli[1], D. Compagnone[2], M. Sergi[2], R. Curini[1]
[1]Department of Chemistry, Sapienza University of Rome, Piazzale A. Moro, 5 – 00185 Roma
[2]Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Via Lerici 1 – 64023 Mosciano Sant'Angelo

New psychoactive substances (NPS) are today a worldwide growing concern; over 500 new substances are currently being monitored by the European Monitoring Center for Drugs and Drug Addiction (EMCDDA) [1]. Sample of drug users as well as deceased persons in fatal events are analyzed for the determination of common illicit drugs, but in many cases even if NPS are present, they are likely to go undetected. There is, then, a need to adapt or to develop analytical strategies to detect these new compounds [2].
The aim of this work was the development of a target method based on liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS) to determine simultaneously several NPS belonging to the classes of synthetic cannabinoids and synthetic cathinones, directly on whole blood in the absence of anti-coagulants. The extraction consists in a partial protein precipitation (PPT) followed by micro solid phase extraction (µSPE) clean-up. The µ-SPE procedure involves standard pipette tips, with a loosely sorbent packed on the edge. Both the sample and the solvents for washing and elution flow through the tip, without the need for vacuum. Scaling down the conventional clean-up techniques allows the reduction of sample volume and organic solvent, leading to a cheaper, quicker and environment-friendly analysis [3].
µSPE was compared with classical techniques such as PPT and LLE in term of recoveries and matrix effect and was shown to provide clean samples in a reduced time. The analysis was carried out by means of LC-MS/MS and data acquisition was operated in multi reaction monitoring (MRM) mode in order to identify at least two product ions for each analyte required as identification points for validation purposes. The method was then validated according to SWGTOX guidelines.

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NEW PSYCHOACTIVE SUBSTANCES (NPS): ANALYSIS IN ORAL FLUID BY MEPS–LC–MS/MS

C. Montesano[1], G. Vannutelli[1], R. Curini[1], R.e Rocchi[2], M.C. Simeoni[2], D. Compagnone[2], M. Sergi[2]
[1]Department of Chemistry, Sapienza University of Rome, P.le A. Moro, 5 – 00185 Roma
[2]Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Via Balzarini 1 – 64100 Teramo

In recent years, new molecules, commonly known as "New Psychoactive Substances" (NPS), have appeared in the illicit market; they include, among other, synthetic cannabinoids, cathinones, phenetylamines and piperazines. At the same time alternative matrices such as hair, oral fluids (OF), sweat and meconium, are gaining attention in forensic toxicology. Particularly, several advantages arise by using OF as sample matrix: sampling is easy and not-invasive and for most drugs there is a good correlation between OF drug concentration and degree of impairment [1]. Consequently this matrix is increasingly being used for Driving Under the influence of drugs (DUID) investigations and workplace testing. For OF testing, where sample volume is limited multi analyte procedures are particularly advantageous: analysis of NPS in OF was reported only in a few studies and generally only a small number of analytes belonging to a single chemical class were included [2].
On this ground, the aim of this work was to design, develop and validate a new method for the simultaneous screening and quantification of a large number of NPS, including synthetic cathinones, piperazines, phenetylamines, synthetic cannabinoids and their metabolites, in OF by ultra-high performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS). Clean-up was based on microextraction on packed sorbent (MEPS) a novel miniaturized SPE technique which uses a syringe containing the solid phase inside the barrel [3]. The method was validated as a confirmation method according to SWGTOX guidelines.

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DEGRADATION OF EMERGING CONTAMINANTS IN AQUEOUS MATRIXES BY PHOTOCATALYSIS WITH $W_{10}O_{32}^{4-}$

E. Sarti, L. Pasti, A. Molinari, N. Marchetti, A. Cavazzini
Department of Chemical and Pharmaceutical Sciences, University of Ferrara, Via L. Borsari 46 - 44121 Ferrara (Italy)

Contaminants of emerging concern (CECs), including pharmaceuticals, are frequently detected at low concentrations in natural waters and, even if some of them have not been established as causes of human illness, they can cause adverse effect on biota such as antibiotic resistance [1, 2]. Therefore, it is important to reduce their introduction in the environment by increasing the efficiency of wastewaters treatment plants [3].
This study aims to evaluate the photocatalytic action of decatungstate anion ($W_{10}O_{32}^{4-}$), both in solution and immobilized on modified silica particles, to degrade some pharmaceuticals in aqueous matrix. The target molecules, differing in chemical structure and physico-chemical characteristics, belong to β-blockers (atenolol and propranolol), antibiotics (sulfamethoxazole, trimethoprim, levofloxacin) and antiepileptic (carbamazepine) drugs.
The characteristics of the heterogenized photocatalyst favor the interaction between photoactive sites and the drug molecule. Finally, the heterogeneous photocatalyst can be recycled without a significant loss of efficiency. This is an important finding because the heterogenization of a soluble photo-catalyst has some advantages such as increase of stability, easiness of recover and handling.
The degradation process has been studied at ambient temperature, atmospheric pressure and at pH values similar to that of natural waters. Stability and reuse of the employed heterogeneous photocatalyst were also examined. EPR spin trapping technique and HPLC-MS analyses gave evidence that the degradation is mediated by $OH^{\bullet}$ radicals.

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MINIATURIZED QuEChERS APPROACH COUPLED TO FAST GC-QqQ MS FOR THE QUANTIFICATION OF PESTICIDES IN DIFFERENT VEGETABLES

A. Schepis[1], M. Zoccali[2], G. Purcaro[2], P. Q. Tranchida[1], L. Mondello[1,2,3]
[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università degli Studi di Messina, Viale Annunziata - 98168 Messina
[2] Chromaleont S.r.l., Viale Boccetta, 70 - 98122 Messina
[3] Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, via Álvaro del Portillo 21, 00128 - Rome, Italy

The QuEChERS (quick, easy, cheap, effective, rugged, and safe) methodology is an emerging sample preparation technique, proposed for the first time in 2003. Since then several modifications have been proposed to adapt the method to different matrices. The method has become the most widespread approach for the analysis of pesticides in agricultural products, since easy and cheap. The main object of the present work was to speed up the entire analytical approach, miniaturizing the preparation step and performing a faster GC determination. Two miniaturized QuEChERS approaches (according to the matrix type) for the extraction and clean-up processes of 35 target pesticides in vegetable products namely tomatoes, zucchini, red peppers and lettuce were proposed. Fast GC coupled to QqQ MS was used for qualitative and quantitative purposes. To confirm the feasibility of the miniaturized developed methods a comparison with the official European Union one, namely EN15662:2008, was carried out. Fully validation of the developed methods was performed considering: matrix effect, recovery, linearity, precision, accuracy, limits of detection (LOD) and quantification (LOQ). To obtain a fast GC run time, an optimal separation of the target compounds, and to reach the European maximum residue limits (MRLs), a microbore non polar column with the following dimension 15 m × 0.10 mm ID × 0.10 mm d_f was used. The recoveries were in the 67.2-123.9% and 70.0-125.5% range respectively for the two miniaturized methods with a %CV in the 0.6-16.1% and 2.1-12.5% range. Linearity was measured using matrix-matched solutions for each sample and evaluated with the Mandel's fitting test (Fcalc<Ftab) in the 10-5000 μg Kg^{-1} range for most compounds, in 15 cases the upper limit was ≈ 1000 μg Kg^{-1}. The developed fast GC-QqQ MS method, fulfills the terms of EU regulation and was applied for the analysis of 35 pesticides in 20 different vegetable samples.

NOVEL ION SOURCE COATINGS FOR LIQUID CHROMATOGRAPHY–ELECTRON IONIZATION MASS SPECTROMETRY

F. Bianchi[1], N. Riboni[1], L. Magrini[2], M. Careri[1], A. Cappiello[2]
[1]Dipartimento di Chimica, Università di Parma, Parco Area delle Scienze 17/A, 43124 Parma
[2]Dipartimento di Scienze della Terra, della Vita e dell'Ambiente, Università degli Studi di Urbino "Carlo Bo", Piazza Rinascimento 6, 61029 Urbino

LC-MS direct-electron ionization (EI) is a recent technique that couples the performance of LC-MS with the advantages deriving from the use of an EI source [1]. Searchable mass spectra are generated, thus allowing to perform an automated library search and to identify unknown compounds.
The vaporization surface of an electron ionization MS source is a key parameter for the detection and characterization of target and untargeted compounds especially for those characterized by high-molecular weight that require high-source temperatures to be correctly detected. Adsorption and thermal degradation phenomena on the stainless steel surface of the EI source can cause peak tailing, thus affecting peak detection. Recently, great efforts have been done to develop inert sources able to increase analyte vaporization and to obtain signal improvements [2].
The use of sol-gel technology can be proposed as a valid alternative to the commonly utilized coating procedures [3] owing to its capabilities of producing a great variety of coatings by operating under mild conditions.
In this study, silica (TEOS)-, titania- and zirconia- based materials were synthesized and tested as new ion source coatings for the determination of polycyclic aromatic hydrocarbons and steroids. All the developed materials were characterized by a very good thermal stability with negligible weight losses until 350-400°C. Excellent results were obtained by using the TEOS-based coating: a noticeable improvement of the vaporization of the investigated analytes was obtained for both PAHs and hormones. Analytes could be detected by operating at low ion source temperatures, i.e. 250°C and no problems related to peak tailing or signal delay were observed.

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HPLC-MS CHARACTERIZATION OF MULTIMODAL LIPID BASED NANOPARTICLES FOR MEDICAL IMAGING

C. Martano[1,3], S. Ghiani[1], F. Ferretti[1], M. Boccalon[2], C. Medana[3], A. Maiocchi[1]

[1]Centro Ricerche Bracco, Bracco Imaging S.p.A., Via Ribes, 5- 10010 Colleretto Giacosa (TO), Italy
[2]Centro Ricerche Bracco, Bracco Imaging S.p.A., AREA Science Park. Ed. Q- S.S. 14 Km 163.5-34149 Basovizza (TS), Italy
[3]Department of Molecular Biotechnology and Health Sciences, Via Nizza, 52-10126 Torino, Italy

In the last decades, different classes of multi-functionalized nanocarriers have been developed in order to deliver imaging reporters to a specific pathological tissue. The increasing attention in the development of these multifunctional nanomaterials is principally due to nanoparticles versatility offered over the conventional agents. In fact, the availability of several surface properties, unique magnetic characteristics and tunable energy absorption and emission properties make the nanoparticles an exciting opportunity on the whole imaging techniques. Nevertheless, imaging probes based on nano-sized systems are still lacking in the clinical market despite to the uncountable engineered nanoplatforms that have been investigated at preclinical level. This is partially due to the great complexity in the manufacturing of highly stable biocompatible nano-suspensions and to the lack of standardized test methods for their characterization [1]. Taking all the above into consideration, there is an increasing need to assess analytical strategies useful to rapidly control nanoparticles formulations and enable easily measurements of their medium and long-term stability. In particular, we focused our attention on Solid Lipid Nanoparticles (SLNs) [2], a biocompatible nano-sized system formulated with several lipid based compounds (i.e. triglycerides, fat acids and phospholipids). Optimized multi-modal SLNs were developed loading with high payload an amphipilic Gd(III) based complex and Indocyanine Green (ICG) for possible applications in magnetic resonance, optical or photo-acoustic imaging. The present work is focused on the analytical characterization of these nano-system and on the examination of its long-term chemical stability by HPLC-MS technique. Accordingly, an HPLC-MS method able to separate and detect all the SLNs components in a single analytical run was assessed. The chemical stability of SLNs was studied storing the formulation at 4°C and speeding up the aging process keeping the same formulation at higher temperature and in different conditions. Possible degradation, oxidation and/or hydrolysis products of each SLNs component in the formulation were hence evaluated.

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MS FRAGMENTATION AND PHOTOINDUCED TRANSFORMATION OF NICOTINE AND COTININE.

P. Calza[1], C. Sala[2], F. Dal Bello[2], M. Pazzi[1], M. Sarro[1] and C. Medana[1]
[1] Dipartimento di Chimica, Università di Torino, via P. Giuria 5-10125 Torino
[2] Dipartimento di Biotecnologie e Scienze per la Salute, University of Torino via P. Giuria 5-10125 Torino

Nicotine and cotinine are respectively an alkaloyd produced mainly by the Solanaceae plant family, especially tobacco, and its most important human metabolite. These compounds are frequently found as new contaminants in wastewater or landfill analysis and they could be used to evaluate tobacco use.
The purpose of this study was the characterization of nicotine and cotinine ESI fragmentation pathways by using HPLC coupled with a high resolving power mass analyzer (LTQ-orbitrap) and the application of these knowledge to the structural identification of photocatalytic transformation products of these two alkaloids.
The transformation of nicotine and cotinine and the formation of intermediate products were evaluated adopting titanium dioxide as photocatalyst besides photolysis experiments. Several products were formed and characterized using the HPLC-HRMS^n technique. The main photocatalytic pathways involving nicotine and cotinine appear to be hydroxylation, demethylation and oxidation. No common degradants were identified.
The evolution of toxicity as a function of the irradiation time was also studied using a bioluminescent photobacterium (*Vibrio fischeri*) test. These new findings could be of interest in further metabolism and environmental pollution studies.
A good likeness of photocatalytic transformation and human metabolism of nicotine was deduced. An endeavour of analytical determination of identified transformation products in river water and landfill percolate did not evidence their presence.

DETERMINATION OF 8 POLYPHENOLS AND PANTOTHENIC ACID IN EXTRA-VIRGIN OLIVE OIL SAMPLES BY A FAST, HIGH-THROUGHPUT AND SENSITIVE UHPLC-MS/MS METHOD

B. Bolfi[1], F. Gosetti[1], M. Manfredi[1], G. Calabrese[2], E. Marengo[1]
[1]Università del Piemonte Orientale, Dipartimento di Scienze e Innovazione Tecnologica, viale T. Michel 11 - 15121 Alessandria
[2]Università di Napoli Federico II, Dipartimento di Farmacia, Via D. Montesano 49 – 80131 Napoli

One of the most important ingredients in Mediterranean diet is Extra virgin olive oil (EVOO), obtained from the first cold processing of the fruits of olive trees only through a mechanical process. Its relevance has grown in years because of its medical, nutritional and cosmetic benefits. Those properties are ascribable to its minor components, polyphenols, also used as an index to evaluate EVOO quality. This work deals with the identification and quantification of 8 polyphenols (hydroxytyrosol, catechin, epicatechin, epigallocatechin gallate, oleuropein, quercetin, rutin, tyrosol) and panthotenic acid through a new ultra-high performance liquid chromatography coupled with tandem mass spectrometry method. In order to be suitable for the analysis, the samples are extracted through a liquid-liquid method using ethanol/water 70/30 and hexane in order to remove the fatty component. The method was validated considering LOD, LOQ, linearity range, intra- and inter-day precision, recovery and matrix effect [1]. The developed UHPLC-MS/MS method is characterized by a high sensitivity due to the correct combination of the stationary phase and mobile phase. Furthermore, the required time for the entire analysis is only ten minutes, taking onto account also the column equilibration time. The separation of nine analytes is satisfactory and further advantages are provided by the complete absence of matrix effect and by good recoveries, all greater than 73.3%. Those features make the method attractive for routine analysis.

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STRUCTURAL CHARACTERIZATION OF INTACT NEUTRAL OLIGOSACCHARIDES AND ALDITOLS BY NEGATIVE ION MALDI MS USING A SUPERBASIC PROTON SPONGE AS DEPROTONATING MATRIX

C.D.Calvano[1,2], T.R.I. Cataldi[1,2], J.F. Kögel[3], A. Monopoli[1], F. Palmisano[1,2], J. Sundermeyer[3]
cosimadamiana.calvano@uniba.it
[1]Dipartimento di Chimica, [2]Centro di Ricerca Interdipartimentale SMART - Università degli Studi di Bari Aldo Moro, via Orabona 4, 70126 Bari (Italy)
[3]Fachbereich Chemie, Philipps-Universitat Marburg, Hans-Meerwein-Straße, 35032 Marburg (Germany)

Although matrix assisted laser desorption/ionization mass spectrometry (MALDI MS) has been recognized as a suitable technique to establish the molecular weights of different saccharides or glycans [1], there are still some challenges due to their inherently low ionization efficiency. Neutral oligosaccharides are usually observed as alkali metal cation adducts in positive ion mode using conventional matrices as 2,5-dihydrobenzoic acid [2]. Coordination to alkali metal cations stabilizes the $[M+Na]^+$ ions and complicates the fragmentation processes, thus limiting sequence information [3]. Indeed, the positive ion spectra are dominated by glycosidic cleavage ions with a resultant unclear and poor assignment for structural characterization. Negative ion fragmentation spectra tend to be much more informative because of the production of abundant cross-ring cleavages and very specific fragmentation pathways [4]. However, neutral saccharides are reluctant to deprotonation unless derivatization reactions are performed.
Here we report the use of a matrix represented by a novel superbasic proton sponge (1,8-bis(tripyrrolidinyl-phosphazenyl)naphthalene (TPPN) [5] capable of abstracting a proton from neutral saccharides. The MS/MS spectra of the resulting $[M–H]^-$ species showed several product ions, mainly due to cross-ring and C-type glycosidic cleavages, which allow more structural information to be obtained. Applications to oligosaccharides, cyclodextrins and alditols are described and discussed.

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PROFILING OF FREE FATTY ACIDS, MONO-, DI- AND TRIACYLGLICEROLS IN A UNIQUE OIL SAMPLE BY A NOVEL HPLC-ESI-Q-ToF METHOD

I. Degano[1], J. La Nasa[1], F. Di Gianvincenzo[1], I. Bonaduce[1]
[1]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Giuseppe Moruzzi, 3, 56124 Pisa, Italy

The profiling of free fatty acids, along with triacylglycerols and intermediate hydrolysis products and possible oxidation materials is a valuable information for those dealing with the characterisation of oils in the food and art research. The profiling and semi-quantitative analysis of di- and triacylglycerols is commonly performed by HPLC analysis, entailing the separation of the analytes on a reverse phase column, interfaced with UV spectrophotometric, evaporative light scattering detection, charged aerosol detector (CAD) or MS detection [1, 2]. Nonetheless, the simultaneous detection of fatty acids and triacylglycerides has seldom been performed, and only in conditions entailing the use of complex elution mixtures and often more than one chromatographic column in series, leading to high back-pressures in the chromatographic system and very long analysis time. The detection of fatty acids by HPLC is generally performed after suitable derivatization reactions, to increase their retention times on RP columns, and to allow their detection by spectrophotometric detectors. These derivatization reactions mostly entail transesterification, and can thus be applied to the free fatty acids extracted from the samples, or after saponification and subsequent acidification and extraction in organic solvents. As a consequence, this strategy is not applicable for profiling of free fatty acids, mono-, di- and tri-glycerides in the same sample.
In this paper, we optimised the derivatization of long chain fatty acids in oil samples with 2-hydrazinoquinoline, whose application for short chain organic acids has been published recently [3]. This reaction does not entail transesterification, thus allowing us to separate and successfully quantify the free fatty acids in the presence of mono-, di- and triacylglycerosl.

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ULTRAHIGH RESOLUTION MASS SPECTROMETRY FOR THE CHARACTERISATION OF WATER SOLUBLE ORGANIC COMPOUNDS IN BIOCHAR

M.Ghidotti[1], D.Fabbri[1], O.Mašek[2], L.Mackay[3], A.Hornung[4]

[1]Dept.Chemistry "G.Ciamician", University of Bologna, Ravenna Campus (Italy); [2]UK Biochar Research Centre, School of Geosciences, University of Edinburgh (UK) [3]School of Chemistry, University of Edinburgh (UK); [4]Fraunhofer Institute- UMSICHT, Branch Sulzbach-Rosenberg (Germany)

The application of biochar in soil is being promoted to address crucial agro-environmental issues related to soil fertility, waste management and carbon sequestration. The increasing use of biochar has promoted the evaluation and standardisation of analytical methods for the determination of priority trace contaminants (e.g. PAHs) [1]. Contamination can arise by the interaction between the vapours generated by pyrolysis and the carbonised biomass during the production of biochar. Besides regulated contaminants, other less investigated organic compounds could be released into the environment during biochar utilisation exerting beneficial or negative effects on plants and soil organisms [2]. In particular, the identification of water soluble organic compounds (WSOCs) and their role in governing biochar toxicity has attracted recent interest [3-4]. To gain new insights into the chemical nature of WSOCs and the relationships with the source of contamination and biochar properties, a set of biochar samples with increasing carbonisation degree were prepared by cornstalk pyrolysis and the corresponding vapours were condensed into bio-oil. WSOCs in biochar and bio-oil water extracts were analysed by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry with Negative Electrospray ionisation (ESI-FT-ICR-MS). Mass spectra of bio-oil confirmed the complex nature of WSOCs with several peaks detected per each nominal mass (*m/z*). Molecular formula assignment allowed the identification of up to 4000 peaks accounting for 80% of total peak abundance with a maximum error of 50 ppb. Species in biochar extracts resembled those in bio-oils with oxygenated compounds (O_{1-15}) comprising the most abundant chemical family. The molecular pattern was correlated with the biochar carbonisation degree (atomic H/C ratio) providing insights useful to drive the correct production of biochar for environmental applications.

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DEVELOPMENT AND VALIDATION OF AN ANALYTICAL METHOD FOR THE CONCURRENT QUANTIFICATION OF QUINOLINIC, PICOLINIC, AND NICOTINIC ACIDS USING AN LC-DAD-QTOF MASS SPECTROMETRY SYSTEM.

I.M. Di Gangi[1], G. Favaro[1], P. Pastore[1]and S. Bogialli[1]
[1]Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo, 1 – 35121 Padova

Quinolinic (QA), picolinic (PA), and nicotinic (NA) acids are "end-products" of the kynurenine pathway from L-tryptophan and are intermediates in the biosynthesis of nicotinamide adenine dinucleotide (NAD). These compounds are involved in complex relationships with inflammatory and apoptotic responses associated with neuronal cell damage and death in the central nervous system. Therefore, they have important contributions to make in clinical and biological research. Among them, quinolinic acid, for example, is believed to be involved in the pathogenesis of several major inflammatory neurological diseases [1,2], whereas PA, is a potent metal-binding ligand with a strong capacity to bind iron and other essential mineral elements [3]. Finally, the water soluble vitamin NA is a primary substrate for the biosynthesis of NAD, a cofactor in energy metabolism, through the tryptophan-NAD pathway, and serves also as a therapeutic agent for its lipid-lowering properties [4]. Thus, the analytical determination of these three acids is therefore of great interest in the selection of potential biomarkers of neurodegenerative diseases.
However, since they are polar compounds, converting into the ionic, neutral or zwitterionic form at different pH, their physical and chemical properties are quite critical in the optimization of analytical methods for the simultaneous quantification of these compounds at low concentrations and in complex matrices [5,6].
Our analytical approach was to evaluate the performance of different columns: such as a PFP core shell Kinetex (Phenomenex), a PolymerX RP-1 (Phenomenex), different type of HILIC (Luna HILIC, Luna NH_2 and Luna CN, Phenomenex) columns, with appropriate chromatographic conditions, in order to find the best compromise for the retention and separation of isomers PA and NA, and in order to accurately quantify all of these compounds by using an LC-diode array detector-quadrupole-time-of-flight (DAD-QTOF) system. Finally, the best solution for this purpose was the use of a porous graphitic carbon column Hypercarb, PGC (Thermo Scientific), in the negative ionization mode, which allows to the retention of these polar compounds thanks to dipole-dipole and ion-dipole interactions with the impurities into the stationary phase.

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DEVELOPMENT AND VALIDATION OF A LC-MS METHOD FOR UNDERIVATIZED AMINOGLICOSIDES ANTIBIOTICS

C. Crescenzi, M. Rodriquez, P. Russo, R.P. Aquino
Dipartimento di Farmacia, Università degli Studi di Salerno, Via Giovanni Paolo II 132, 84084 Fisciano, Salerno, Italy

Aminoglycoside antibiotics are a class of extremely polar analytes that requires ion pair agents in order to be retained on reversed phase HPLC columns. Such conditions generate excellent separation but strongly inhibit MS detection using electrospray interfaces. The ability of porous graphitic carbon HPLC column to retain and separate six popular aminoglycoside antibiotics was investigated using a wide range of chromatographic conditions. The effects of several factors such as solvents, additives, pH, and temperature were deeply investigated. The optimized chromatographic conditions demonstrate to be highly compatibles with electrospray ionization interface. Quality parameters were assessed as well as robustness. Detection limits were ranged in picograms level. The method was validated on real sample. The possibility of using the same conditions for evaporative light scattering as alternative detection techniques was also evaluated

INTERACTIONS OF ACTIVATED PAHS WITH DNA: DETECTION OF ADDUCTS BY MEANS OF MALDI-TOF/MS

M. Sergi[1], F. Di Ottavio[1], M.C. Simeoni[1], C. Montesano[2], A. Pepe[1], D. Compagnone[2]
[1]Faculty of Bioscience and Technology for Food, Agriculture and Environment, University of Teramo, Via Balzarini 1 – 64100 Teramo
[2]Department of Chemistry, Sapienza University of Rome, P.le A. Moro, 5 – 00185 Roma

Covalent modification of DNA by a chemical has been demonstrated to be the initial step in chemical carcinogenesis. The presence of adducts can thus be an useful biomarker both in cancer risk assessment [1].
Recently, different studies have been conducted also on the toxicity of PAHs exposed to UV and visible light: the photodegradation products have been demonstrated to be mutagenic and to induce DNA damage [2]. Detection of DNA adducts is, however, a rather complex matter, because of the low frequency of DNA adduction that occurs in vivo. Mass spectrometric (MS) detection can be an useful tool for the identification of these adducts [3,4]. In this work, the detection of activated PAH–oligonucleotide adducts using MALDI-TOF/MS is reported. In the first part of the work, a procedure for detection of the adducts was developed using B[a]P-dihydrodiol epoxide (B[a]PDE) as model compound. The structures of adducts of B[a]PDE with guanosine and adenosine have been identified and characterized, as well as the adducts with oligonucleotides (GGGG and CCCC). The following step was devoted to the identification and characterization of photodegradation products of B[a]P and the detection adducts with oligonucleotides under the experimental conditions.For this purpose different MALDI matrices were tested in order to achieve best sensitivity due to effective ionization and less interfering peaks.

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Acknowledgements: Project IZS ME 07/13 RC Valutazione del rischio chimico tossicologico degli integratori alimentari connesso alla presenza di idrocarburi policiclici aromatici IPA.

TWO-DIMENSIONAL FT-ICR MS FOR TOP-DOWN PROTEOMICS: A MULTIDIMENSIONAL STUDY ON CALMODULIN

F. Floris[1], M.A. van Agthoven[1], L. Chiron[2], C.A. Wootton[1], Y.P.Y. Lam[1], M.P. Barrow[1], M-A. Delsuc[2,3], P.B. O'Connor[1]
[1]University of Warwick, Coventry, UK
[2]CASC4DE, Illkirch-Graffenstaden, France
[3]IGBMC, Illkirch-Graffenstaden, France

Two-dimensional Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (2D FT-ICR MS) allows data independent fragmentation of all ions in a sample and correlation of fragment ions to their precursors through the modulation of precursor ion cyclotron radii prior to fragmentation. Previous results show that implementation of 2D FT-ICR MS with InfraRed MultiPhotoDissociation (IRMPD) and Electron-Capture Dissociation (ECD) has turned this method into a useful analytical tool. In the last decade, 2D FT-ICR MS has been used to analyse small molecules, such as cholesterol, and macromolecules such as cytochrome c and collagen, using a bottom-up approach. In this work, 2D FT-ICR MS is developed and implemented for the top-down analysis of Calmodulin (CaM) and compared with its bottom-up approach. Furthermore, a multi-fragmentation MS^3 experiment called MS/2D MS is developed. In MS/2D MS quadrupole ion selection is used to select a precursor charge state for Calmodulin, which is fragmented using Collisional Activation (CAD) in the hexapole collision cell. The fragments are then subjected to IRMPD or ECD for further fragmentation, and the result is a two-dimensional map showing the whole MS^3 of Calmodulin in a unique experiment.

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CHECKING ETHANOL CONTENT IN BIOFUELS USING AN ORGANIC PHASE ENZYME ELECTRODE (OPEE) WORKING IN DECANE.

M. Tomassetti, G. Spuri Capesciotti, R. Angeloni, E. Martini, M.P. Sammartino, L. Campanella.
Dipartimento di Chimica, Università di Roma "La Sapienza", p.le Aldo Moro, 5, 00185 Roma.

Actually small concentrations of Ethanol are contained in leadless petrol used as fuel for cars. Whereas higher concentrations of ethanol are contained in biofuels, already used in several countries of the American continent. The aim of the present research work was the use of new biosensor, recently developed by our research group, to determine the ethanol content of biofuels [1]. The new sensor is also quite peculiar: it is a 'substrate competition' OPEE (Organic Phase Enzyme Electrode), working in decane, in which the enzyme catalase is coupled to an amperometric gaseous diffusion Clark type oxygen electrode. This innovative biosensor is based on two parallel oxidative reactions in competition, both of which catalysed by the same enzyme catalase in the presence of the same hydroperoxide substrate (tertbutylhydroperoxide) working in decane. Two reactions are the following:

$$tbuOOH + O_2 + 2RH \xrightarrow{catalase} tbuOH + 2RO + H_2O \quad (1)$$

$$tbuOOH + CH_3CH_2OH \xrightarrow{catalase} tbuOH + CH_3CHO + H_2O \quad (2)$$

In practice, the reciprocal of the ratio between the current variations, or the oxygen concentrations, recorded after the addition of hydroperoxide alone (reaction 1) and after the addition also of ethanol (reaction 2), respectively, is found to correlate with the concentration of the added ethanol. Since the organic solvent used is involved in the enzymatic reaction (1), where is indicated as RH, the choice of solvent is of decisive importance. The catalase biosensor was previously optimized and characterized, than used to determine ethanol concentration in the first time, in leadless petrols [1]; while at present this OPEE was employed to check the ethanol content in two biofuels samples. The concentration values obtained were compared with values given by the producer firms. In order to assess any interference due to the complexity of the matrix, recovery tests were performed using the 'standard addition method', obtaining satisfactory results. In conclusion, the results obtained show that this biosensor method may be used to determine the ethanol content of biofuels, as the measures performed are comparatively rapid, precise and relatively selective, lastly the biofuel samples tested do not need to be pretreated.

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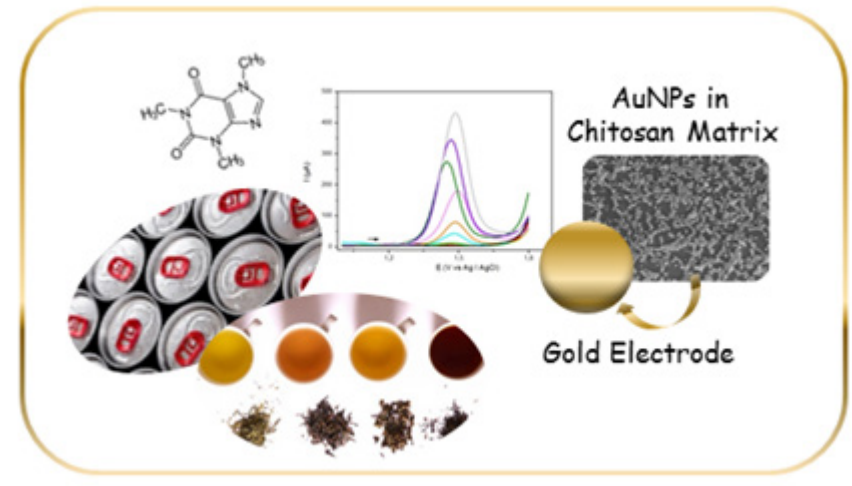
DETERMINATION OF CAFFEINE @ GOLD NANOPARTICLES MODIFIED GOLD (AU) ELECTRODE

A. Trani[1], D. Zane[1], R. Petrucci[2], G. Marrosu[2]-and A. Curulli [1]
[1] CNR SMN Istituto per lo Studio dei Materiali Nanostrutturati UOS Sapienza Via del Castro Laurenziano 7 00161 Roma (Italy)
[2] Sapienza Università di Roma, Facoltà di Ingegneria Civile e Industriale, Dip. SBAI, Via del Castro Laurenziano 7, 00161 Roma
e-mail antonella.curulli@ismn.cnr.it

A simple and selective method for the determination of caffeine has been developed at a gold modified electrode. The electrochemical behaviour of caffeine at a bare gold electrode and at a gold electrode modified with gold nanoparticles was carried out in acidic medium by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). Electrochemical parameters were studied in order to evaluate the possible sensor performance improvement.
The most satisfactory results were obtained with a gold electrode modified with gold nanoparticles, stabilized into a chitosan matrix, in aqueous solution containing $HClO_4$ 0.4 mol L^{-1} as supporting electrolyte. The range of linearity, the stability, the reproducibility, the limit of detection (LOD) and the response to a series of interfering compounds, especially present in natural beverages, were evaluated. The sensor was successfully used to determine the caffeine content in commercial beverages and results were compared with those obtained with HPLC-PDA as an independent method and with those declared from manufacturers.



MICRO-FLOW IMMUNOSENSOR BASED ON THIN-FILM INTERDIGITATED GOLD ARRAY MICROELECTRODES FOR CANCER BIOMARKER DETECTION

A. Ravalli[1], L. Lozzi[2], G. Marrazza[1]
[1]Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, Via della Lastruccia, 3 – 50019 Sesto Fiorentino (FI)
[2]Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila, Via Vetoio, 95125 Coppito (AQ)

In this work, we reported the development of a micro-flow label-free impedimetric biosensor based on the use of thin-film interdigitated gold array microelectrodes (IDA) for the detection of carbohydrate antigen 125 (CA125) [1]. IDA electrodes presents the advantages of the microelectrodes features increasing the sensitivity and the detection limits and, coupled with micro-fluidic system, allow the development of automatic device with easy data analysis, easy handling of chemicals (solution replacing and washing steps), the use of low volume of solutions which results in an increase of the precision and the accuracy of the measurements. Furthermore, due to the use of micro in-flow cell, both the mass transfer (from the mediator to the electrode surface) and the radial flow are increased which results in an improvement of the electrochemical response. IDA electrodes are also suitable for the use together with electrochemical impedance spectroscopy (EIS): this technique allows the estimation of bioreceptor-antigen affinity reaction without the use of a label which reduce the time and the costs of the analysis. In particular, the immunosensor is developed through the electropolymerization of anthranilic acid (AA) on the surface of IDA electrodes followed by the covalent attachment of anti-CA125 monoclonal antibody. CA125 protein affinity reaction was then evaluated by means of electrochemical impedance spectroscopy (EIS). The sensor was characterized by electrochemical techniques and scanning electron microscopy (SEM). Using the optimized experimental conditions, the developed immunosensor showed a good analytical performance for CA125 detection from 10 to 100 U/mL with estimated limit of detection of 7 U/mL.

ROOM TEMPERATURE CHEMORESISTIVE SENSOR FOR THE DETECTION OF AMMONIA AND TRIMETHYLAMINE

C. Paoletti[1], P. Salvo[1], N. Calisi[1], B. Melai[1], A. Pucci[1], F. Di Francesco[1]
[1]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Giuseppe Moruzzi, 13 – 56124 Pisa

Fish consumption has steadily increased in the last decades due to its flavour and health benefits. At the same time, fish is the most perishable flesh food and its rapid degradation represents a major issue for its trade. The odour provides a first indication for freshness, since fish flesh releases increasing amounts of characteristic volatile compounds during degradation, such as for example ammonia (NH_3) and trimethylamine (TMA). Fresh fish releases up to 10 ppm of TMA, whereas concentrations between 10 and 50 ppm indicate a preliminary rot and concentrations over 60 ppm a rotten product. The consumption of altered fish can cause serious health problems.
Due to the large variability in the spoilage attitude among different species, harvests and fishes of a same catch, the fishing industry and agencies for the food safety have always shown interest in methods for the fast evaluation of fish freshness. This interest increased after regulation of food traceability, which implies the need to assess quality and identify the responsibility of the correct storage along the whole food chain. Accurate portable devices are needed to measure NH_3 and TMA in the field, as they would help to prevent the degradation of products and allow quality controls at each transfer of product between different actors of the distribution chain.
In this work, we show the functionalization of single-walled carbon nanotubes (SWCNTs) with different moieties to develop chemoresponsive materials for the detection of NH_3 and TMA. The functionalization with 4-azido-2,3,5,6-tetrafluorobenzoic acid produced the most sensitive SWCNTs in the range 5 - 80 ppm. Such sensitive material was manually integrated in a Radio Frequency Identification (RFID) tag. The electronic circuit of the tag was disrupted by punching the aluminum track between the integrated circuit and the capacitor, then the electrical connection was reactivated by drop-casting the responsive material in the gap. Our prototype operates at room temperature and represents a very promising smart device for a cost-effective onsite chemical detection of gas molecules.

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DEVELOPMENT OF SILICON-BASED MATERIALS FOR SENSORS APPLICATIONS

C. Zanardi, G.Lusvardi, R. Seeber
Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via G. Campi 103, 41125 Modena, Italia,
chiara.zanardi@unimore.it

Silicate-based is the most important inorganic polymer. Among the various routes proposed for its synthesis, the sol-gel technology offers important advantages, namely the use of mild experimental conditions (e.g low temperatures) and the possibility to obtain homogeneous materials, characterized by high porosity and low density. The high porosity allows the inclusion of various chemical species within the polymer matrix.
Amperometric sensors based on sol-gel matrices are highly performant and, at the same time, cheap. When used for such an application, a suitable amount of graphite should be inserted within the polymer matrix to increase the conductivity of the resulting material. The advantage to use such a material in amperometric sensing is that the electroactive surface can be very simply and rapidly renewed by a mechanical cleaning procedure.
In the recent past,[1] we have discussed the advantage of the inclusion of a graphite/Au nanoparticles (AuNPs) composite in the sol-gel matrix, replacing the use of simple graphite grains. The composite is effective in activating electroactive processes, that can be exploited for glucose and H_2O_2 determination. In this case, the synthesis of AuNPs was carried out in a step preceding the actual formation of the composite.
In this communication we discuss the performance of sol-gel based electrodes containing a different graphite/AuNPs composite. In this case, AuNPs are obtained concomitantly to the synthesis of the sol-gel. To such a purpose, a suitable amount of a Au(III) salt is added to the solution containing the silane precursor, namely trimethoxyethylsilane; the formation of AuNPs is achieved by thermic treatment of the resulting silicon-based material. Electrochemical, spectroscopic and microscopic analyses have been carried out in order to define the physico-chemical properties of the material at varying the experimental conditions used for the synthesis of the material. Furthermore, the performance of the resulting electrodes has been evaluated with respect to the non-enzymatic determination of glucose.

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POTENTIOMETRIC SENSOR FOR THE NON INVASIVE LACTATE DETERMINATION IN HUMAN SWEAT

M. Onor[1], T. Lomonaco[2], S. Ghimenti[2], S. Gufoni,[3] F. Sorrentino[3,4] and E. Bramanti[1]

[1] National Research Council of Italy, C.N.R., Istituto di Chimica dei Composti Organo Metallici-ICCOM- UOS Pisa, Area di Ricerca, Via G. Moruzzi 1, 56124 Pisa (Italy)

[2] Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 1, 56124 Pisa (Italy)

[3] Marwan Technology Srl, via L. Gereschi 36, 56127 Pisa, Italy

[4] Istituto Nazionale di Fisica Nucleare, sezione di Genova, via Dodecaneso 33, 16146 Genova, Italy

The present work describes a noninvasive lactate sensing in sweat during workout. The sensing system is based on a potentiometric measure performed using disposable, chemically modified, printed electrodes (sensor strips) that can be wetted with sweat during the exercise. The potentiometric signal, which is proportional to lactate concentration in sweat, is produced by a redox reaction activated by UV radiation, as opposed to the enzymatic reaction employed in traditional, blood-based measuring devices. The sensing system exhibits chemical selectivity toward lactate with linearity from 1 mM up to 180 mM. Differently from other recent methods published [1], The dynamic linear range is suitable for measurement of lactate in sweat, which is about 10 times more concentrated than hematic lactate and reaches more than 100 mM in sweat during workout. The noninvasive measure can be repeated many times during exercise and during the recovery time in order to get personal information on the physiological and training status as well as on the physical performance.

The device was successfully applied to several human subjects for the measurement of sweat lactate during prolonged cycling exercise. The measured changes of lactate concentration during the exercise reflected the intensity of physical effort. During the exercise sweat was simultaneously sampled on filter paper and extracted in water, and the lactate was determined by HPLC for method validation. This method has perspectives in many sport disciplines as well as in health care and biomedical area.

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DETECTION OF OKADAIC AND DOMOIC ACID IN SEA WATER BY COLORIMETRIC ASSAYS

K. Petropoulos, G. Volpe, S. Piermarini, L. Micheli, G. Palleschi
Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica 1 - 00133 Roma.

In the frame of SMS project, aimed to develop a novel automated networked system for *in situ* monitoring of marine water contaminants in coastal areas, we are developing two colorimetric assays for the detection of Okadaic acid (OA) and Domoic acid (DA).
OA is a lipophilic marine toxin produced by *Dinophysis* and *Prorocentrum*, and is responsible for causing diarrheic shellfish poisoning (DSP) to humans after ingestion of contaminated shellfish. So, an early detection of OA, directly in marine water, is an important aspect for public safety and natural environment. The mechanism of action of OA is based on the inhibition of protein phosphatase type 2A (PP2A). The degree of inhibition of the PP2A enzyme can be used as a measure of toxin concentration. In this work we present the recent experiments performed to assess the specificity of the PP2A assay, previously set up by our research group. The study was carried out by testing OA-group toxins, such as *dynophysis* toxins (DTX-1 and DTX-2, the only commercial available), and other algal toxins (palytoxin, domoic acid and saxitoxin). The results showed that only OA, DTX-1 and DTX-2 exhibited an inhibitory activity against PP2A, demonstrating the ability of the method to selectively detect this class of marine toxins.
DA is a naturally occurring neurotoxin produced by several species of marine diatoms from the genus *Pseudo-nitzschia* and is responsible for causing a human intoxication syndrome known as amnesic shellfish poisoning (ASP), characterized by severe gastrointestinal and neurological disorders. For this reason, its measurement in seawater could be an early alert for potential toxin accumulation in marine organisms.
Preliminary results of a direct competitive ELIMC (Enzyme-Linked Immuno-Magnetic Colorimetric) assay for the detection of DA is also presented in this work. Free DA and DA-HRP conjugate compete towards a monoclonal anti-Domoic Acid antibody, immobilized on the surface of magnetic beads (MBs, pre-coated with IgG anti-mouse). The MBs, covered with the immunological chain, are then dissolved in a solution that contains 3,3,5,5-tetra-methybenzidine and hydrogen peroxide, as enzyme substrates. The activity of the captured enzyme is spectrophotometrically detected at 450nm. In the presence of DA, competition occurs and consequently the rate of color production decreases proportionally to the concentration of the toxin.

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A MINIATURISED NAFION-BISMUTH-SENSOR FOR EVALUATING THE MARINE ORGANISM *S. PLICATA* BIOREMEDIATION CAPACITY TOWARD HEAVY METAL POLLUTED SEAWATER

N. Colozza[1], F. Arduini[1], M. F. Gravina[2], L. Amendola[3], M. Rosati[3], G. Palleschi[1], D. Moscone[1]
[1]Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma "Tor Vergata", Via della Ricerca Scientifica, 1 – 00133 Roma
[2]Dipartimento di Biologia, Università degli Studi di Roma "Tor Vergata", Via della Ricerca Scientifica, 1 – 00133 Roma
[3]Arpa Lazio, Via G. Saredo, 52 – 00173 Roma

Cadmium and lead are known to be among the most polluting heavy metals because of their persistence in the environment and toxicity for living organisms. They can be released in small amount from natural processes, but the largest quantities discharged into the environment are from anthropic origin, causing serious pollution.
Filter-feeding organisms can be used to bioremediate polluted aquatic environment, as they are able to capture toxic chemicals within the gills structure during their natural filtering activity, and to bioconcentrate them in the tissues. In this work we studied the bioremediation capacity of a marine filter-feeding organism, *S. plicata* (Tunicata, Ascidiacea), in seawater artificially polluted with known quantities of Cd^{2+} and Pb^{2+}. To our knowledge, an estimation of its capacity to bioconcentrate Cd^{2+} and Pb^{2+} in controlled conditions have not yet been investigated. Thus, a bioremediation experiment was elaborated and monitored by measuring Cd^{2+} and Pb^{2+} concentration in seawater and *S. plicata* tissues with a miniaturised sensor. This sensor is based on a screen-printed electrode modified *in situ* with a bismuth film, which favors the concentration of the heavy metals on the working electrode surface and avoids the use of the traditional but much more toxic mercury-based electrode.[1] A Nafion film is then added, to provide protection against fouling due to organic compounds.
The detection of Cd^{2+} and Pb^{2+} was optimised by using square wave anodic stripping voltammetry, obtaining satisfactory detection limits for both the metals (LOD: 0.3ppb for Pb^{2+}; 1.5ppb for Cd^{2+}). The sensor showed the capability to reveal Cd^{2+} and Pb^{2+} at ppb level in both seawater and biological tissues, giving results consistent with the ones obtained by spectrometric analysis. Finally, it was demonstrated that *S. plicata* has slight capacity to bioremediate Cd^{2+} and Pb^{2+} polluted seawater (bioconcentration factors: 7 for Cd^{2+}; 15 for Pb^{2+}).
In conclusion, the resulting sensor showed to be suitable as a screening device for polluted marine environments and for the bioremediation monitoring.

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SERUM CHOLINESTERASE ACTIVITY DETECTION BY USING AN INNOVATIVE MICROFLUIDIC PAPER-BASED DEVICE

G. Scordo, F. Arduini, S. Cinti, G. Palleschi, D. Moscone
Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma "Tor Vergata", Via della Ricerca Scientifica, 1 – 00133 Roma

Cholinesterase is an enzyme present in nervous tissue and muscle, and being able to catalyze hydrolysis of acetylcholine to choline and acetic acid. Acetylcholine is released when a nerve impulse reaches a myoneural junction, it diffuses across the synaptic cleft and binds to cholinergic receptors on the muscle fibers, causing them to contract.
Since the detection of Cholinesterase activity is a crucial issue in clinical field, several analytical methods are reported in literature[1], however they require laboratory set-up and are not suitable for point-of-care analysis.
Herein, we developed a rapid and easy to use microfluidic paper-based device (μPAD) for cholinesterase activity measurement.
We printed solid wax patterns on office paper, consecutively melted on a hot plate allowing wax penetrates the full thickness of the paper. The use of wax patterns confers to the office paper generating several hydrophobic and hydrophilic regions, as well. Successively, working, counter, and reference electrodes were printed on the hydrophilic region.
To measure Cholinesterase activity, the enzymatic by-product thiocholine was detected using a printed sensor modified with carbon black and Prussian Blue nanoparticles (CB/PBNPs). Using these paper based electrodes and cyclic voltammetry, we have observed the electrocatalysis of CB/PBNPs, demonstrating the suitability of this hybrid nanocomposite for the detection of thiocholine at low applied potential. Finally, Cholinesterase activity was quantified in amperometric mode with an applied potential of +200 mV using 15 minutes as reaction time, and substrate at concentration of 10 mM. Preliminary studies highlighted the effectiveness of novel μPAD towards the detection of diverse levels of Cholinesterase units giving useful information about clinical status of the patient.

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AN SPR CHEMOSENSOR BASED ON MOLECULARLY IMPRINTED POLYMER ON PLASTIC OPTICAL FIBER FOR FOOD APPLICATION

M. Pesavento[1], N. Cennamo[2], L. Zeni[2], D. Merli[1], D. Pastran[1], S. Marchetti[1]

[1]Dipartimento di Chimica, Università degli Studi di Pavia, Via Taramelli, 12 – 27100 Pavia
[2]DIII, Seconda Università di Napoli, Via Roma, 29 -81031 Aversa

Furfural (furan-2-carbaldehyde, 2-FAL) derives from the de-hydration of pentose and from the Maillard reaction, so it is widely present in different foodstuffs, particularly those treated at high temperature. The rapid and low cost determination of furfural in food, as wine [1], bear, fruit juice, honey, vegetal oil, is of increasing interest not only for its technological relevance, included the fact that 2-Fal, and in general the furanic derivatives, have been proposed as ageing or inappropriate storage conditions markers, but also to its possible toxic and carcinogenic effect on the human beings.
Sensors are analytical devices particularly suited to this aim. The sensor for 2-FAL here proposed consists of a synthetic receptor for 2-FAL, i.e. a specific molecularly imprinted polymer (MIP), and of a new SPR transduction method, based on plastic optical fiber (POF), which is particularly suited to sensor application, due to the very low dimension and low cost [2]. It is based on the determination of the refractive index variations at the interface between a metal layer (a gold layer 60 nm thick in this case) and a dielectric, i.e. a layer of MIP deposited directly over the gold layer.
Due to the use of optical fiber, the resonance wavelength is measured instead of the classical resonance angle. The refractive index variation, measured as a shift of the resonance wavelength, is induced by the combination of 2-FAL with the specific sites on the MIP layer. The resonance wavelength was shifted to higher values upon adsorption of 2-FAL on MIP, indicating that the refractive index of the polymer increases. The dependence of the wavelength variation ($\Delta\lambda$) on concentration was not linear, so that the experimental data were fitted by the Langmuir isotherm.
The proposed sensor is able to selectively detect the presence of furfural in water at concentration from about 0.1 to 10 μM, which is of interest for food control.

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GOLD NANOPARTICLE-ENZYME ASSEMBLY FOR ENVIRONMENTAL BIOSENSORS

S. Rella[1], M.G. Manera[2], R. Rella[2], C. Malitesta[1]
[1] Laboratorio di Chimica Analitica, Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali (DiSTeBA), Università del Salento, Lecce – Italy
[2] IMM-CNR, Istituto per la Microelettronica e Microsistemi, Lecce, Italy

Nowadays, optical devices sensitive to both inorganic and organic pollutants are subject of study and research in view of their application in those sites where a continuous monitoring is required in the biomedical or environmental or industrial field. The high interest in those matters is due to the great number of possible opportunities offered by the modern technology. They include a variety of optical techniques already consolidated in chemical and biochemical analysis fields, the availability of materials and components borrowed from optoelectronic technologies which are in great expansion, allowing to develop extremely flexible systems thanks to the availability of miniaturized optical waveguides.
The main objective to be pursued is the realization of an optical biosensor based on enzyme inhibition for the detection of pollutants in environmental samples.
The dynamic monitoring of the presence of chemical pollutants (responsible for the enzymatic inhibition) could be carried out by means of an optical investigation in the visible spectral range by monitoring the variation of the plasmonic peak typical of gold nanoparticles immobilised onto glass substrates[1,2].
In this work, we report a preliminary study about the development of metal (gold) nanoparticles chemically anchored by means of appropriate surface treatments onto glass substrates. In particular, glass substrates has been modified through different chemical silanization[3] strategies to optimize the adhesion of colloidal gold nanoparticles suitable to generate a plasmonic transducer for biosensing application.

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ON-CHIP LAMP-BART REACTION FOR VIRAL DNA REAL-TIME BIOLUMINESCENCE DETECTION

M. Zangheri[1], M. Mirasoli[1], F. Bonvicini[2], N. Lovecchio[3], G. Petrucci[3], D. Calabria[1], A. Nascetti[4], D. Caputo[3], G. Gallinella[2], A. Roda[1], G. De Cesare[3]
[1]Department of Chemistry "Giacomo Ciamician", Alma Mater Studiorum - University of Bologna, via Selmi 2, 40126 Bologna, Italy
[2]Department of Pharmacy and Biotechnology, Alma Mater Studiorum - University of Bologna, via Belmeloro 6, 40126 Bologna, Italy
[3]Department of Information, Electronics and Communication Engineering, Sapienza University of Rome, via Eudossiana, 18, 00184, Rome, Italy
[4]Aerospace Engineering School, Sapienza University of Rome, via Salaria, 851/881, 00138, Rome, Italy

The development of miniaturized analytical devices suitable for the quantitative detection of markers of infection or pathology in biological samples in point-of-care (POC) setting is one of the hardest challenges in analytical chemistry. To obtain accurate diagnosis of infectious diseases, real-time quantitative nucleic acids amplification and detection is the gold standard, providing low limits of detection, rapidity, reliability of results, and reduced contamination issues. In particular loop-mediated isothermal amplification (LAMP) is emerging as a very promising technique, offering high specificity, sensitivity, rapidity and simple detection of amplification products.
The present study describes the development of an integrated lab-on-chip, in which viral DNA amplification is carried out under constant temperature (65°C) by means of LAMP amplification. Quantitative information on target DNA is obtained by means of the real-time bioluminescence detection of LAMP products, exploiting the bioluminescent assay in real-time (BART) technology.
Specifically, a LAMP-BART technique was optimized to specifically amplify and quantitatively detect parvovirus B19 (B19V) DNA.
The lab-on-chip, integrating all the elements necessary for temperature control and on-chip detection, is based on thin film technology. In particular, it is a glass substrate hosting on one side a thin-film metal heater and on the other side hydrogenated amorphous silicon (a-Si:H) diodes, which act as temperature and light sensors. The a-Si:H photosensors provide the real-time monitoring of the bioluminescence signal through the amplification.
All the reagents are contained in a disposable 10-µL polydimethilsiloxane (PDMS) chamber, designed to ensure optimal thermal and optical coupling. A dedicated electronics is employed to control the chip temperature and photons detection along the whole experiment.
Assay and chip design and performance will be reported.

SMARTPHONE-BASED BIOSENSOR INTEGRATING BIOLUMINESCENT "SENTINEL CELLS" FOR EFFECT-BASED ANALYSIS

M.M. Calabretta[1], L. Cevenini[1], E. Michelini[1,2], G. Tarantino[1], A. Lopreside[2], A. Roda[1,2]
[1]Department of Chemistry "G. Ciamician", University of Bologna Via Selmi, 2, Bologna
[2]INBB, Istituto Nazionale di Biostrutture e Biosistemi, Viale Medaglie d'Oro 305, Roma.
[3]Centro Interdipartimentale di Ricerche sul Cancro "Giorgio Prodi", Via Masserenti 9, Bologna

Global security threats have become a major concern and their early detection represents a major challenge to current monitoring technologies. The routine monitoring of water, food and the environment for chemical and biological threat agents is often hampered by the fact that available techniques usually require clean samples and sophisticated equipment based on high performance liquid chromatography-tandem mass spectrometry and are thus unsuitable for real-time, cost-effective and on-field routine monitoring. We report a compact stand-alone toxicity sensor incorporating bioluminescent cells into a smartphone-based device. We fabricated 3D printed cartridges to integrate an array of bioluminescent cells into ready-to-use cartridges and smartphone adaptor. We used human embryonic kidney cells (Hek293T) constitutively expressing a green-emitting luciferase as "sentinel cells" and an Android app was developed to provide a user-friendly built-it data analysis. To confirm the suitability of this approach the toxicity test showed performance comparable to that obtained using portable cooled CCD camera. The analytical performance of the smartphone-biosensor was evaluated with model and real samples [1]. We also explored the feasibility of using as reporter genes both Nanoluc and its destabilized version NlucP; dose-response curves for Tumor Necrosis Factor α, used as pro-inflammatory analyte, showed the same limit of detection (0.4±0.1 ng/ml) and an EC50 of 1.3±0.4 ng/ml and 1.7±0.2 ng/ml for Nluc and NlucP, respectively. Conscious that huge efforts will be required to extend the lifespan of the integrated cells without affecting the analytical performance of the system, we believe that it could find significant application as rapid alerting tool, suitable for detecting the presence of harmful pollutants in civil and military water supplies, for terrorism surveillance, and for detection of health threats in drinking water in developing countries.

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COMPETITIVE AMPEROMETRIC IMMUNOSENSOR FOR DETERMINATION OF p53 PROTEIN IN URINE SAMPLES AS RAPID AND NONINVASIVE SCREENING TOOL FOR EARLY DIAGNOSIS OF BLADDER CANCER

M. Giannetto[1], M.V. Bianchi[2], M. Mattarozzi[1], M. Careri[1]
[1]Dipartimento di Chimica, Università degli Studi di Parma, Parco Area delle Scienze, 17/A – 43124 Parma
[2]Dipartimento di Bioscienze, Università degli Studi di Parma, Parco Area delle Scienze, 11/A – 43124 Parma

p53, a potent transcription factor that is activated in response to different stresses and environmental insults, can be considered as a biomarker of crucial importance in diagnostic and for the optimization of therapeutic strategies [1]. It serves important defence mechanism against cancer onset and progression, acting as a 'guardian of the genome'. To date, diagnostic techniques used for its determination require long run times and high costs. A valid alternative approach is represented by biosensors, which are small, portable devices, easy-to-use, and give rapid and quantitative results. The purpose of the present study is the development of a diagnostic device, based on disposable nanostructured substrates, for the determination of the p53 protein, as clinical evidence of cancer.
The immunosensor was implemented on disposable "Screen-Printed" Carbon Nanotubes-Gold Nanoparticles Electrodes (CNT-GNP SPCEs) [2]. The presence of carbon nanotubes confers porosity to the material, increasing the available area to bind the receptor to working electrode, while gold nanoparticles involve the formation of covalent bonds by means of chemisorption of the proteins on their surface. We decided to focus our attention on a competitive format assay [3]. A two-factor three-level experimental design was used to determine the best conditions in terms of signal inhibition. Detection and quantification limits calculated according to Eurachem guidelines, were assessed at 0.1 and 0.4 μg/mL, respectively.
Studies currently in progress are focused on validation of the device in real samples of clinical concern, such as urine, in order to apply the immunosensor as rapid and non-invasive screening tool for early diagnosis of bladder carcinoma.

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SWAN-ICARE: A SMART WEARABLE AND AUTONOMOUS NEGATIVE PRESSURE DEVICE FOR WOUND MONITORING

B. Melai[1], N. Calisi[1], P. Salvo[1], C. Paoletti[1], E. Herrera[1], A. Kirchhain[1], V. Mollica[1], R. Fuoco[1] and F. Di Francesco[1]
[1]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via G. Moruzzi, 13 – 56124 Pisa

The EU FP7 SWAN-iCare project aims at developing an integrated autonomous device for the monitoring and the personalized management of chronic wounds, mainly diabetic foot ulcers and venous leg ulcers. Most foot and leg ulcers are caused by diabetes and vascular problems respectively but a remarkable number of them are also due to the co-morbidity influence of many other diseases (e. g. kidney disease, congestive heart failure, high blood pressure, inflammatory bowel disease). More than 10 million people in Europe suffer from chronic wounds, a number which is expected to grow due to the aging of the population. The core of the project is the fabrication of a conceptually new wearable negative pressure device equipped with Information and Communication Technologies. Such device will allow users to: (a) accurately monitor many wound parameters via non-invasive integrated micro-sensors, (b) early identify infections and (c) remotely provide an innovative personalized two-line therapy via non-invasive micro-actuators to supplement the negative pressure wound therapy. This paper describes the main components of the SWAN-iCare system and its potential impact in the area of wound management.

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DETECTION OF POLYBROMINATED DIPHENYL ETHERS (PBDES) BY USING AN ELECTROCHEMICAL IMMUNOASSAY

F. Bettazzi[1], T. Martellini[1], W.L. Shelver[2], A. Cincinelli[1], E. Lanciotti[3], I. Palchetti[1]
[1] Dipartimento di Chimica, Università degli Studi di Firenze, Via della Lastruccia, 3-50019 Sesto Fiorentino, Firenze
[2] USDA-ARS Biosciences Research Laboratory, 1605 Albrecht Boulevard, Fargo, ND 58102, USA
[3] Dipartimento di Scienze della Salute (DSS), Università degli Studi di Firenze, Viale Morgagni, 48- 50134 FIRENZE

Polybrominated diphenyl ethers (PBDEs) are persistent environmental substances that have been commonly used as fire retardants in a wide number of commercial products. Their low reactivity, high hidrophobicity and bioaccumulative properties cause their ubiquity in the air, water, food and lead to extensive exposure of world population to these compounds. The severe health problems caused by PBDEs lead to be banned from the market. In March 2014 the European Commission issued a recommendation in which member states are requested to monitor brominated flame retardants in food, in order to evaluate human and wildlife exposure.
Here, we described the development of an electrochemical magnetic particle enzyme-linked immunoassay (ELISA) to analyze PBDEs in food samples. The immunological reaction is based on a competitive scheme, using an alkaline phosphatase (AP) labelled congener as tracer. The anti-PBDE antibody modified magnetic particles are captured on the surface of carbon disposable array of sensors. The reaction extent is finally electrochemically measured by differential pulse voltammetry (DPV), upon the addition of substrate. Under the optimized conditions, a LOD of 0.18 ng/mL with a LOQ of 0.30 ng/mL and a quantification range of 0.30- 6.9 ng/mL, (RSD%= 12) is obtained. Results of food samples obtained from the newly developed electrochemical immunoassay are also reported [1].

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SILICA-SUPPORTED g-C_3N_4 AS A NEW SORBENT FOR SOLID-PHASE EXTRACTION OF FLUOROQUINOLONES FROM ENVIRONMENTAL WATERS

A. Speltini[1], F. Maraschi[1], R. Govoni[1], C. Milanese[1], A. Profumo[1], L. Malavasi[1,2], M. Sturini[1]
[1]Dipartimento di Chimica, Università di Pavia, via Taramelli 12, 27100 Pavia, Italy
[2]Dipartimento di Chimica, Università di Pavia, e INSTM, via Taramelli 12, 27100 Pavia, Italy

Graphitic carbon nitride (g-C_3N_4) is the newest carbon-based 2D material and shows a "graphene-like" structure of layered sheets of tri-s-triazine connected via tertiary amines. g-C_3N_4 is considered a very promising carbon material for solid-phase extraction (SPE) applications [1]. In this work silica-supported g-C_3N_4 was tested for SPE of fluoroquinolone (FQ) pollutants from water. FQs are a major class of emerging contaminants, and their diffusion in environmental waters is reason of great concern [2]. g-C_3N_4, prepared by one-pot thermal condensation of dicyandiamide, was first characterized by XRD, TGA, SEM, FTIR and BET surface area measurements, and then applied as sorbent for SPE of the most used human and veterinary FQs from water, prior HPLC-FD. The extraction efficiency of g-C_3N_4 was tested in tap and raw surface waters (spike 10-100 ng L^{-1}). Quantitative adsorption was achieved using 100 mg sorbent (20 wt% g-C_3N_4) for pre-concentration of 50-500 mL sample, working at the native pH. Elution was performed with 25 mM H_3PO_4 aqueous solution-acetonitrile (80:20), obtaining recoveries in the range 70-101%, enrichment factors up to 500 and inter-day RSDs ≤ 12%. The batch-to-batch reproducibility was assessed on 3 independently synthesized g-C_3N_4@silica preparations (RSDs 6-12%). Silica-supported g-C_3N_4 proved to be of easy and costless preparation compared to the recently proposed graphene-derivatized silica [3], and was reusable for at least 4 extractions of real samples. The overall analytical procedure sensitivity (MQLs 10-20 ng/L) was comparable or even better than the one reported for the most recent carbon-based sorbent phases.

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EXTRACTION OF ESTROGENIC COMPOUNDS IN WATER WITH POLYDOPAMINE-COATED MAGNETIC NANOPARTICLES FOR UHPLC-MS/MS ANALYSIS

C. Cavaliere, P. Foglia, G. La Barbera, R. Samperi, S. Ventura, A. Laganà
Dipartimento di Chimica, Università di Roma "La Sapienza", Piazzale Aldo Moro 5, 00185 Roma

A multiresidue analytical method for the determination of seventeen natural estrogenic compounds, including four steroid estrogens, six mycoestrogens and seven phytoestrogens, in river water samples has been developed. (Fe3O4)-based magnetic nanoparticles coated by polydopamine (Fe3O4@pDA) were used for dispersive solid phase extraction, and the final extract was analyzed by ultra-high performance liquid chromatography coupled with tandem mass spectrometry.
The Fe3O4@pDA magnetic nanoparticles were prepared by a co-precipation procedure, coated by pDA, and characterized by scanning electron microscopy, infrared spectroscopy and elemental analysis.
The sample preparation method was optimized in terms of extraction recovery, matrix effect, selectivity, trueness, precision, method limits of detection and quantification (MLOQs). For all the seventeen analytes, recoveries were >70% and matrix effects were below 30% when 25 mL of river water sample were treated with 90 mg of Fe3O4@pDA nanoparticles. Selectivity was tested by spiking river water samples with other fifty compounds (mycotoxins, antibacterials, conjugated hormones, UV filters, alkylphenols, etc.); only aflatoxins and some benzophenones showed recoveries >60%. Moreover, the in situ polymerization of pDA on MNP core has been shown to be facile and reproducible from batch to batch.
In this work, we have proved the ability of pDA to selectively capture estrogens and structurally similar compounds, i.e., mycoestrogens and phytoestrogens, from river water samples. Even if the importance of phytoestrogens as environmental contaminants has been reported, however, generally these substances are not included in multi-residue methods for estrogenic compounds. Therefore, in this work, we wanted to fill this gap using magnetic SPE for the simultaneous determination of these three groups of estrogens in river water. Moreover, the obtained MLODs and MLOQs are lower than those reported in the literature for estrogens and mycoestrogens using the same pDA-coated MNPs.

PHTHALATES DETERMINATION IN DIFFERENT BEVERAGE MATRICES BY DISPERSIVE LIQUID-LIQUID MICRO-EXTRACTION COUPLED WITH GC-IT/MS

M.V. Russo[1], P. Avino[2], I. Notardonato[1]
[1]Dipartimento Agricoltura, Ambiente e Alimenti, Università degli Studi del Molise, via De Sanctis - 86100 Campobasso
[2]DIT, INAIL Settore Ricerca, via Roberto Ferruzzi, 38/40 - 00143 Roma

Since the 1950s phthalates (PAEs) are largely used in polymers to enhance the flexibility and extensibility of the materials. Because these compounds are reported to act as endocrine disruptors, and the exposure at high levels can cause harmful effects in the human reproductive system, their determination in food and beverages are fundamental due to their use as food/beverage containers and packaging.
Various pretreatment techniques followed by chromatographic analysis have been developed to analyze PAEs from different samples: among them, the dispersive liquid-liquid microextraction (DLLME) is very interesting and powerful. It is based on the addition of an immiscible solvent showing higher density to the aqueous sample for extraction step. In order to concentrate apolar molecules in the dispersed phase it is also essential to add a dispersant solvent which increases the contact between the two immiscible solvents, and having the characteristics to be soluble in both. The interface plays an important role in the extraction process and its development is facilitated by adding just the disperser solvent [1].
This communication would like to show the application of such extraction protocol to different beverage matrices at different alcoholic content (from 5 alc vol^{-1} to 45 alc vol^{-1}) or recreational beverages (soft drinks, coffee, etc.): using a single extraction protocol followed by GC-IT/MS is possible to analyze DMP, DEP, DBP, BcEP, BBP, DEHP in such matrices.
All the analytical parameters will be investigated and discussed. In particular, the role of the vortex step is largely discussed: this step allows to enhance the recoveries (between 95 % and 103 %). On the other hand, Enrichment Factors range between 258 and 300 whereas LODs and LOQs are adequate for determining such compounds at trace and ultra-trace levels in such samples. Further, applications to real samples will be reported.
Finally, some comments on the applicability of this methodology to the determination of other organic pollutants will be introduced preliminarily.

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EXTRACTION OF CROCINS FROM SAFFRON USING MOLECULARLY IMPRINTED POLYMERS

A.A. D'Archivio[1], M. A. Maggi[2], F. Ruggieri[1]
[1]Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila, Via Vetoio, 67010 Coppito, L'Aquila, Italy
[2]Hortus Novus, Via Collepietro, 67100 L'Aquila, Italy

Crocins, the mono- and di-glycosyl esters of crocetin, are water-soluble carotenoids responsible for the colouring power of saffron. More than 20 compounds, differing in the *cis* or *trans* isomeric form of crocetin and in the kind of the sugar moieties (glucoside, gentiobioside, neapolitanoside or triglucoside), have been identified in saffron.
We have synthetized a molecularly imprinted polymer using as template the mixture of crocins naturally occurring in saffron (croc-MIP). To increase the concentration of the template molecules, a saffron ethanolic extract was preliminarily purified by crystallisation. This procedure also resulted in the elimination of the other main ingredients of saffron, such as safranal and picrocrocin. HPLC was used to evaluate the extraction efficiency and selectivity of croc-MIP and, for comparison, of a polymer imprinted with D-gentiobiose (gent-MIP), a non-imprinted polymer (NIP) and two common commercial cartridges packed with polymeric or C_{18} stationary phases. The individual behaviour of the major crocins was investigated by batch adsorption experiments and by application of the above materials as solid phase extraction (SPE) sorbents. Moreover, SPE based on croc-MIP was applied to saffron samples with the aim of reducing the interference due to the crocins in the analysis of selected triazine herbicides by means of HPLC with photometric detection.

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BUILDING OF AN LC-EI-MS DATABASE, INCLUDING LINEAR RETENTION INDEX (LRI) DATA, FOR ACHIEVING A FAST AND RELIABLE IDENTIFICATION IN LIQUID CHROMATOGRAPHY

F. Rigano[1], M. Russo[2,3], P. Dugo[1,2,3], L. Mondello[1,2,3]
[1]Chromaleont S.r.L., Viale Boccetta 70, 98122 Messina, Italy
[2]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, Via Alvaro del Portillo 21, 00128 Rome, Italy
[3]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali - University of Messina - Polo Annunziata, Viale Annunziata, 98168 Messina, Italy

The present research focus on the object to improve identification capability in liquid chromatography (LC), by creating a system as similar as possible to GC one, where the combination/complementarity of Linear Retention Index (LRI) [1] and Electron Ionization Mass Spectrometry (EI-MS) data makes the identification process easy, automatic and reliable.
Particularly, in LC the untargeted characterization of real-world samples is still a challenge, due to the not repeatable and poorly informative nature of typical atmospheric pressure ionization mass spectrometry (API-MS) data, normally hyphenated to LC. On the contrary, electron ionization (EI) MS, being a hard fragmentation technique, is characterized by a very extensive fragmentation pattern, which can represent the fingerprinting of a molecule. Furthermore, EI occur in the gas phase under high vacuum conditions, so that any molecule-ion or molecule-molecule interaction is avoided, thus preventing any matrix effect. Because of the clear benefits arising from EI technique, the aim to hyphenate LC with EI-MS has never been abounded, major obstacle being the compatibility of the LC effluent with the high vacuum region of the ion source. In the last decades the miniaturization of LC instrumentation together with the considerable progresses in MS vacuum pump capability has made such hyphenation more feasible.
Furthermore an LRI system in LC is here proposed, based on the use of an alkyl aryl ketone homologue reference series (from acetophenone to heptanophenone, C8-C13) for LRI calculation, as reported in literature [2,3].
In order to evaluate both the LC-EI-MS coupling performance and the feasibility of the LRI identification system in LC, typical and well-known LC-amenable samples, namely Citrus essential oils have been injected for the detection of the oxygen heterocyclic compounds.

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QUANTIFICATION OF MINERAL OIL CONTAMINATION IN VEGETABLE OILS BY MEANS OF GAS CHROMATOGRAPHY AFTER AN EFFICIENT REMOVAL OF OLEFIN INTERFERENCES BY USING ON-LINE LIQUID-LIQUID CHROMATOGRAPHY

A. Schepis[1], M. Zoccali[2], G. Purcaro[2], M. Beccaria[2], D. Sciarrone[1], L. Mondello[1,2,3]

[1] Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Polo Annunziata, Viale Annunziata - 98168 Messina

[2] Chromaleont S.r.l., Viale Boccetta, 70 - 98122 Messina

[3] Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, via Álvaro del Portillo 21, 00128 - Rome, Italy

Mineral oils (MOH) are a complex mixture of compounds, primarily manufactured from crude petroleum through distillation processes and various refining steps, mainly consisting of saturated (MOSH) and aromatic (MOAH) hydrocarbons. MOAH can reach 10-30% of the MOSH content and are of potential concern for human health due to their carcinogenic effect. Vegetable oils can be contaminated with mineral oils from different sources. Liquid chromatography coupled to gas chromatography (LC-GC) with flame ionization detection (FID), represents the method of choice for the analysis of these two families. However, it is important to highlight that, the lack of mass spectrometry (MS) detection, due to the frequent controversies about the effective nature of the chromatographic hump, makes these determinations an hard task. Moreover, a correct quantification of the MOAH fraction can be affected by the presence of olefins, particularly squalene and its isomers, which can reach 5000 mg/kg in olive oils. In the present work, a novel on-line LC-GC method with a double detection [FID and triple quadrupole (QqQ) MS] were employed for the determination of hydrocarbon contamination in edible oils. Two different LC columns were coupled in series: a silica column to retain the bulk of the matrix (triglycerides) and to separate MOSH and MOAH, followed by a silver-ion one, which retains olefins allowed to obtain a MOAH hump free of interfering peaks. The QqQ MS system was used to evaluate the presence of hopanes as markers of petrogenic origin of the MOH contamination.

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ULTRA PERFORMANCE CONVERGENCE CHROMATOGRAPHY FOR FOOD LIPID CHARACTERIZATION: TOWARDS FASTER AND GREEN ANALYSIS

V. Inferrera[1], P. Donato[2], F. Cacciola[2], P. Dugo[1,3,4], L. Mondello[1,3,4]
[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Polo Annunziata, Viale Annunziata - 98168 Messina
[2]Dipartimento di Scienze Biomediche, Odontoiatriche e delle Immagini Morfologiche e Funzionali, Università degli Studi di Messina, Viale Consolare Valeria - 98165 Messina
[3]Chromaleont S.r.l., Viale Boccetta, 70 - 98122 Messina
[4]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, via Álvaro del Portillo 21, 00128 - Roma

Supercritical fluid chromatography (SFC) has increased its acceptance between scientists during the last decade; its unique selectivity, short analysis times, low consumption of organic solvents and the improvements in instrumentation have contributed to expand its use when individualized evaluation of several compounds in very complex samples is required. From the perspective of current applied research, Ultra Performance Convergence Chromatography (UPC^2), combining the use of CO_2 with sub-2 μm particle columns, is complementary to gas and liquid chromatography (LC), in terms of speed and reproducibility of analysis. The miscibility of CO_2 with a variety of polar and non-polar organic solvents has made UPC^2 versatile enough to separate a wider range of compounds than reversed-phase LC.
A systematic approach to the study of vegetable oil samples is here illustrated, in which the hyphenation to mass spectrometry (UPC^2-MS) is enabling new ways of separating non-polar lipids, like triacylglycerols (TAGs), with substantial advantages over conventional LC methods. Different oils were analyzed, varying in their TAG composition and complexity, i.e. palm, olive, peanut, corn, soybean, and borage. While the number of positive identifications (around 80 TAGs in borage oil) was comparable to what reported in the literature, run time was drastically reduced (>10 times) and also the organic solvent consumption (>30). The use of an atmospheric pressure chemical ionization interface alleviates the need for a post-column make-up solvent/pump, thus retaining the advantages of a less toxic, and environmental-friendly technique.

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(LOW-)FLOW MODULATION COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY FOR THE DETERMINATION OF SUSPECTED ALLERGENS IN FRAGRANCES

M. Maimone[1], F. A. Franchina[2], G. Purcaro[2], P. Q. Tranchida[1], L. Mondello[1,2,3]
[1]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali - University of Messina - Polo Annunziata, Viale Annunziata, 98168 Messina, Italy
[2]Chromaleont S.r.L., Viale Boccetta 70, 98122 Messina, Italy
[3]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, Via Alvaro del Portillo 21, 00128 Rome, Italy

Several different analytical methods based on GC-MS are used for the determination of fragrance allergens in raw materials and cosmetic products in accordance with EU Directive 2003/15/EC. Rather recently, a new opinion from Scientific Committee on Consumer Safety (SCCS) proposed a new list, increasing the number of suspected allergic substances.
From an analytical point of view, two-dimensional GC is preferred for complex perfume samples, in which possible co-elution of target allergens with other compounds can occur.
In this contribution, a comprehensive capillary GC method coupled to quadrupoleMS is presented for the analysis of the new suspected allergens proposed by the SCCS (opinion SCCS/1459/11).
The method was applied to perfume samples containing several regulated allergens. The multidimensional system employed a flow modulator operating at low flows, directing all the D^2 effluent to the MS.

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DETAILED CHARACTERIZATION OF COMPLEX NATURAL MATRICES AND IDENTIFICATION OF UNKNOWN COMPOUNDS TO BE ADDED INTO A DEDICATE DATABASE FOR THE FLAVOUR AND FRAGRANCE FIELD

G. Micalizzi[1], M. Utczás[1], G. Purcaro[1], D. Sciarrone[2], L. Mondello[1,2,3]
[1]Chromaleont S.r.l., Viale Boccetta, 70 - 98122 Messina
[2]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, University of Messina, Polo Annunziata, viale Annunziata, 98168 – Messina
[3]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, Via Alvaro del Portillo 21, 00128 - Roma

The studies of natural samples for the characterization and possibly isolation of unique compounds to be used in the nutraceutical, pharmaceutical and flavour & fragrance field is of high interest.
Gas chromatography coupled to mass spectrometry (GC-MS) is the technique of choice a detailed characterization of any kind of complex sample. In fact, the reliability of the MS spectra generated by the electron impact (EI) ionization has allowed the creation of wide databases for simplify the identification approach. However, sometimes this approach can fail due to the presence of isomers with practically the same MS spectrum, or due to the lack of the specific spectrum. The use of the Linear Retention Indices (LRI) approach, used in combination with conventional mass spectral search boosts the identification of ambiguous molecules when a certain degree of separation is reached in GC. Otherwise, the support of alternative analytical techniques are necessary to identify and isolate the specific compounds. In the present research, compounds not present in the commercial libraries were isolated from different distilled oils (e.g. Clausena lansium and Cordia verbenacea) and fully characterized with the aim of GC coupled to Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). The completely characterized compounds were then injetced in a GC-MS system and the MS spectra were added to a database dedicated to the flavour and fragrance field, namely FFNSC library. Each compound is registered in the database, along with structural information, IUPAC name, CAS number, and the experimental value of LRI. The latter have been obtained utilizing three different types of reference standards (n-alkanes, fatty acid methyl esters and fatty acid ethyl esters) and three different stationary phases (1% and 5% diphenyl-95% polymethylsiloxane, polyethyleneglycol).

CHARACTERISATION OF THE VOLATILE AND NON-VOLATILE FRACTION IN PROCESSED AND NATIVE *ARBUTUS UNEDO*

M. Utczás[1], G. Purcaro[1], F. Cacciola[2], D. Giuffrida[2], L. Mondello[1, 3,4]
[1]Chromaleont S.r.l., Viale Boccetta, 70 - 98122 Messina
[2]"Dipartimento di Scienze Biomediche, Odontoiatriche e delle Immagini Morfologiche e Funzionali", University of Messina, - Polo Annunziata - viale Annunziata, 98168 – Messina, Italy
[3]"Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali", University of Messina, - Polo Annunziata - viale Annunziata, 98168 – Messina, Italy
[4]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, Via Alvaro del Portillo 21, 00128 - Roma

The *Arbutus unedo* is an evergreen shrub native in the Mediterranean region and in France and Ireland. Its fruit and nectar are widely used for the preparation of honey, jam and liqueurs.
Volatile and non-volatile fraction of the fresh fruit of *Arbutus unedo* and its honey and jam were studied. The volatile fraction of each sample was characterized by mean of mono- and bi-dimensional gas chromatography coupled to mass spectrometry (GC or GC×GC-MS) after sample preparation with head-space solid phase microextraction. Identification of the unknown compounds was carried out with a GC-MS database dedicated to the flavour and fragrance field, namely FFNSC library. The latter support the reliable identification of complex samples, since not only the mass spectra similarity but also the linear retention index information are used for peak assignment. The effect of the food process on the volatile fraction profile was investigated quantitatively and qualitatively comparing the natural fruit and the other final commercial products. The non-volatile fraction containing bioactive molecules was also examined by mean of high performance liquid chromatography (HPLC) coupled to mass spectrometry using atmospheric pressure chemical ionisation.

EMBEDDED LINEAR RETENTION INDICES IN MS SPECTRA DATABASE: RELIABILE IDENTIFICATION OF COMPLEX SAMPLES IN THE FLAVOUR AND FRAGRANCE FIELD

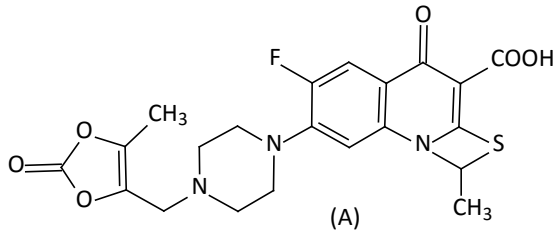
M. Utczás[1], G. Micalizzi[1], G. Purcaro[1], L. Mondello[1, 2,3]
[1]Chromaleont S.r.l., Viale Boccetta, 70 - 98122 Messina
[2]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, University of Messina, Polo Annunziata, viale Annunziata, 98168 – Messina
[3]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, Via Alvaro del Portillo 21, 00128 - Roma

Gas chromatography coupled to mass spectrometry (GC-MS) is a powerful analytical method for a detailed characterization of any kind of complex sample. A commercial spectra database can be a useful support for identifying unknown substances, but in many cases misidentification can occur due to a high spectral similarity. Conventional mass spectral search using also the Linear Retention Indices (LRI) approach can provide a great possibility to boost the identification of "challenging" molecules, occurring in flavours and fragrances. To use reliably the LRI information it is important to know exactly the GC column stationary phase and the chromatographic conditions. A GC-MS database devoted to the flavour and fragrance field, namely FFNSC library, collecting around 3500 spectra derived from pure chemicals, essential oils and perfumes, has been built-up. The quadrupole MS spectrum of each compound is registered in the database, along with structural information, IUPAC name, CAS number, and the experimental value of LRI. The latter have been obtained utilizing three different types of reference standards (n-alkanes, fatty acid methyl esters and fatty acid ethyl esters) and three different stationary phases (1% and 5% diphenyl-95% polymethylsiloxane, polyethyleneglycol). To maximize the potentiality of such a database, the use of a post-run software, CromatoPlus Spectra, was exploited. This software allows to import data coming from different systems and to perform the identification with the simultaneous support of the spectra similarity and the LRI filter. It has been proven that a LRI filter in the ± 5 range allows to perform a highly reliable identification of complex samples.

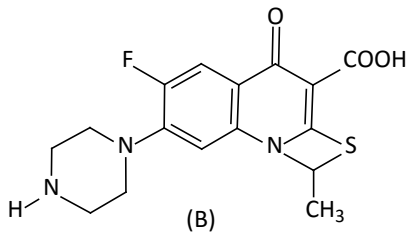
A SIMPLE METHOD FOR THE DETERMINATION OF ULIFLOXACIN THE ACTIVE METABOLITE OF PRULIFLOXACIN IN HUMAN PLASMA AND URINE OF PATIENTS WITH PERIPHERAL ARTERIAL DISEASE BY MEPS-UHPLC-PDA

V. Ferrone[1], M. Carlucci[2], S. Genovese[1], P. Palumbo[3], G. Carlucci[1]
[1]Dipartimento di Farmacia, [2]Dipartimento di Scienze Mediche Orali e Biotecnologiche - Università degli Studi "*G. d'Annunzio*" Chieti-Pescara, via dei Vestini 31 – 66100 Chieti-Italy, [3]Dipartimento di Medicina Clinica, Sanità Pubblica, Scienze della Vita e dell'Ambiente, Università degli Studi di L'Aquila - 67100 L'Aquila, Italy

A novel sensitive analytical method based on the use of a semi-automatic microextraction by packed sorbents (MEPS) techniques combined with ultra high-performance liquid chromatography (UHPLC) with PDA detection has been developed and validate for the analysis of ulifloxacin (B), the active metabolite of prulifloxacin (A) using danofloxacin as internal standard in human plasma and urine. Different experimental parameters were optimized and validated according to international guidelines. Complete separation of the analytes was achieved with a Waters BEH C_{18} (50 x 2.1 mm I.D.,1.7 μm particle size) analytical column, a mixture of 10mM ammonium acetate (pH 3.0) (A) with and acetonitrile (B) both containing 1% triethylamine were used as mobile phase, at a flow rate of 0.6 mL/min in gradient elution, and detection wavelength of 272 nm. This method is linear in concentration range of 0.02 - 10.0 μg/mL for plasma and urine, respectively. The limit of quantitation was 20 ng/mL for the two fluids. The recoveries of the method were 95% for ulifloxacin in human plasma and urine and 95.5% for the internal standard. Intra- and inter- assay precision and accuracy for ulifloxacin were lower than 10% at all tested concentrations.



(A)



(B)

This method will be subsequently used to quantify the drugs in patients with PAD to establish if the dosage regimen given is sufficient to eradicate the infection at the target site[1].

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ISOLATION OF UNKNOWN MOLECULES FROM PLANT EXTRACTS EXPLOITING A MULTIDIMENSIONAL GC-PREP SYSTEM FOLLOWED BY NMR, MS AND FTIR FOR STRUCTURAL IDENTIFICATION

D. Sciarrone[1], L. Mondello[1,2,3]

[1] "Scienze chimiche, biologiche, farmaceutiche ed ambientali" Department, University of Messina, Messina, Italy
[2] Chromaleont s.r.l., c/o "Scienze chimiche, biologiche, farmaceutiche ed ambientali" Department, University of Messina, Messina, Italy
[3] University Campus Bio-Medico of Rome, Roma, Italy

The continuous research for novel molecules represents nowadays a "hot topic" for many academic and industrial fields as pharmaceutical, nutraceutical and flavour & fragrance just to consider some of them. The never-ending availability of new plant species from all over the world for example can be considered one of the most important of source for new molecules. Obviously, the staring point for any possible application in each industrial or research field is the structure elucidation of such molecules in order to investigate possible biological functionality or other uses. As well known, natural samples are often characterized by a high complexity composition therefore any elucidation step often suffers the presence of interfering molecules that can hinder a clear identification of molecules of interest. Moreover, once identified, synthetic issues can arise when the possible candidate has to be produced in order to carry out biological tests or similar procedures. A possible alternative is the direct isolation of the candidate from the real sample exploiting GC-prep, even if this technique was historically affected by tedious procedures, often with poor productive collections. Recently we proposed a highly productive multidimensional GC-prep system demonstrating the capability to collect highly pure sample amounts (mgs) in a short time. The system can be operated in different configurations, based on the complexity of the sample, exploiting a front-end LC pre-separation (whenever required by the complexity of the sample) and two or three GC dimensions with the aim to purify the fraction of interest prior to the collection step. The present research deals with the isolation and further structural elucidation of unknown molecules from plant extracts by means of NMR, MS and vapour phase FTIR. Different case-of-study are reported describing the potentiality of such an approach to provide a useful starting point for the identification of possible highly valuable molecules for industrial and biological evaluations.

SUPERCRITICAL FLUID CHROMATOGRAPHY×ULTRA HIGH PRESSURE LIQUID CHROMATOGRAPHY WITH ION MOBILITY MASS SPECTROMETRY DETECTION

P. Donato[1], V. Inferrera[2], D. Giuffrida[1], F. Cacciola[1], P. Dugo[2,3,4], L. Mondello[2,3,4]
[1]Dipartimento di Scienze Biomediche, Odontoiatriche e delle Immagini Morfologiche e Funzionali, Università degli Studi di Messina, Viale Consolare Valeria - 98165 Messina
[2]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Polo Annunziata, Viale Annunziata - 98168 Messina
[3]Chromaleont S.r.l., Viale Boccetta, 70 - 98122 Messina
[4]Unit of Food Science and Nutrition, Department of Medicine - University Campus Bio-Medico of Rome, via Álvaro del Portillo 21, 00128 - Rome, Italy

The combination of normal phase (NP) and reversed phase (RP) liquid chromatography (LC) is one of the most effective way to increase the orthogonality in two-dimensional comprehensive LC (LC×LC), being the two separation mechanisms truly independent. However, the NP-LC×RP-LC coupling is not easy and straightforward to implement, mainly related due to the immiscibility of the mobile phases, peak focusing at the head of the secondary column (2D), and peak deterioration.
A viable alternative is to replace the first (1D) NP-LC dimension by supercritical (SFC) or subcritical fluid chromatography; such a combination alleviates immiscibility issues and further provides a number of advantages related to the use of supercritical CO_2. An on-line SFC×RP-LC separation system is here presented implemented in a fully automated fashion around two 2-position, six-port switching valves equipped with two packed octadecyl silica cartridges for effective trapping and focusing of the analytes after elution from 1D. The addition of a water make-up flow to the SFC effluent prior to entering the loops permitted to efficiently focus the solutes on the sorbent material and to reduce interferences of expanded CO_2 gas on the second dimension separation.
Such a platform was demonstrated for the characterization of native carotenoids in a complex paprika sample, with photodiode array and ion mobility mass spectrometry detection. The latter adds more separation dimensions, based on the solute mass, charge, and shape.

Acknowledgements
The authors wish to thank the “University of Messina” for support through the “Research and Mobility” Project.

AN INNOVATIVE ANALITICAL TECHNIQUE: FEXRAV APPLIED ON ALCALINE FUEL CELLS FOR THE INVESTIGATION OF INTERFACE SPECIES

W. Giurlani[1], A. Lavacchi[2], A. Giaccherini[1], F. Di Benedetto[3,4], F. d'Acapito[5] and M. Innocenti[1,2]
[1] Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3, 50019, Sesto Fiorentino (FI), Italy.
[2] CNR, Istituto dei Composti Organometallici, via Madonna del Piano 10, 50019, Sesto Fiorentino (FI), Italy.
[3] CNR, Istituto di Geoscienze e Georisorse, via G. La Pira, 4, 50121, Firenze (Italy)
[4] Dipartimento di Scienze della Terra, Università di Firenze, via La Pira 4, 50121, Firenze (Italy).
[5] CNR, Istituto di Officina dei Materiali, OGG, c/o ESRF, Grenoble (France)

Fuel cells are gradually taking place worldwide in the energetic panorama. These devices need to be understood in depth to improve the extrinsic energy efficiency; for this reason, an innovative analytical technique, focused on the reactions of the electrodic surface for heterogeneous catalytic reactions, has been developed. This technique is called FEXRAV (Fixed Energy X-ray Absorption Voltammetry) and represents an innovative, fast and easy[1] method for the in situ and in operando X-ray absorption analysis. The measurement is taken at LISA Beamline, in the synchrotron of Grenoble, recording the changes in X-ray absorption and/or fluorescence intensity while the electrode potential varies at a fixed of energy. In this way, it is possible to perform conventional electrochemical methods, like cyclic voltammetry, and follow the transition between different valence states of the elements under observation at the same time[2]. The in operando study allows to point out intermediate oxidation states and adsorption species that are not visible in an ordinary cyclic voltammetry; from these information it is also possible to extrapolate an hypothesis about the reaction mechanism. Palladium nanoparticles supported on carbon have been studied in solution of KOH, EtOH and $HCOO^-$ between 0V and 1.2V vs RHE at two different wavelengths. By results, it is possible to detect and quantify the percentage of oxide on the catalyst, the maximum overpotential that a full cell should reach before the poisoning of the catalyst and its loss in function of time; different trends have been recorded in different solutions, suggesting that different reaction mechanisms were taking place.

[1] A. Minguzzi, O. Lugaresi, C. Locatelli, S. Rondinini, F. D'Acapito, E. Achilli, P. Ghigna, Anal. Chem. (2010), 85, 7009-7013.
[2] A. Minguzzi, O. Lugaresi, E. Achilli, C. Locatelli, A. Vertova, P. Ghigna, S. Rondinini, Chem.Sci. (2014), 5, 3591-3597.

STUDY OF THE INTERACTIONS BETWEEN HALLOYSITE NANOTUBES AND KAOLINITE WITH BOVINE SERUM ALBUMIN BY FT-IR SPECTROSCOPY

V. Della Porta[1], B. Campanella[1,2], C. Duce[2], M.R. Tinè[2], E. Bramanti[1]

[1]Istituto di Chimica dei Composti Organometallici - UOS di Pisa, Consiglio Nazionale delle Ricerche (CNR), Via Moruzzi 1 – 56124 Pisa
[2]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13 – 56124 Pisa

During the last few decades, materials based on nanoclays have attracted large interest. Within this field, halloysite nanotubes (HNTs) are newly emerging clays with unique features and appealing perspectives, considered an ideal material for biotechnological and medical applications.
The study of the interaction between nanoparticles/nanotubes and proteins is significant because the modifications that biological molecules undergo upon the interaction with nanostructured materials may alter their function.
Nanoparticles are known to interfere with protein amyloid formation and it is known that protein aggregation into amyloid fibrils is implicated in severe neurodegenerative diseases. Few studies are reported on the conformational changes induced by nanoparticle or nanotubes on the aggregated proteins.
In this work, FTIR spectroscopy has been used to identify the structural changes of proteins induced by the interaction with tubular (HNTs) or flat (kaolinite, Kao) clay surface in order to understand the role of clays morphology in protein conformation.
We shown that the conformational changes of BSA depend on protein concentration, clay morphology and clay/protein ratio. The surface curvature radius seemed to have a big role in the final protein conformation. Both curved nanoscale surface of HNTs and the flat morphology of Kao deeply interfered on the α/β transitions of BSA. This determines also the percentage of protein adsorbed on the clay surface.

FTIR STUDY OF PROTEINS CONFORMATION CHANGES AFTER LOADING INTO HALLOYSITE NANOTUBES

V. Della Porta[1], B. Campanella[1,2], C. Duce[2], M.R. Tinè[2], L. Ghezzi[2], A. Spepi[2], E. Bramanti[1]

[1]Istituto di Chimica dei Composti Organometallici - UOS di Pisa, Consiglio Nazionale delle Ricerche (CNR), Via Moruzzi 1 – 56124 Pisa
[2]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13 – 56124 Pisa

Halloysite nanotubes (HNTs) are newly emerging clays with unique features and appealing perspectives. HNTs are considered a "green" material, which is, in principle, not hazardous for the environment and an ideal material for biotechnological and medical applications.
A remarkable feature of HNTs is its different surface chemistry at the inner and outer sides of the tubes: silica layer is relevant to the outer surface of tube, while the alumina is in the inner surface. Aluminium and silicon oxides have different ionization properties and surface charge: alumina has a positive charge up to pH 8.5, while silica is negative above pH 1.5. This allows for the selective loading of negatively charged molecules inside the HNTs inner surface. Loaded HNTs can be used for the controlled or sustained release of proteins, drugs, bioactive molecules and other agents that could benefit from controlled release.
The study of the interaction between proteins and nanotubes is important for the biotechnological and medical applications because the modifications that biological molecules undergo upon their interaction with nanostructured materials may alter their function.
In the present work, HNTs were loaded with bovine serum albumin (BSA), alpha lactalbumin (α-Lac) and beta lactoglobulin (β-Lg) proteins. The loading procedure was selected on the basis of literature data. FTIR spectroscopy has been used to identify the structural changes of proteins induced by the interaction with HNTs. TGA has been used to study the thermal behaviour of proteins adsorbed on the internal surface of nanotubes.
The interaction of proteins with the inner surface of HNTs causes perturbations of their thermal stability and secondary structure. The interaction and loading of the three proteins with HNTs depends on their initial conformation and isoelectric point. We proposed that electrostatic forces are involved in the mechanism of protein binding to the inner surface of HNTs.

AN INNOVATIVE ANALITICAL TECHNIQUE: FEXRAV APPLIED ON ALCALINE FUEL CELLS FOR THE INVESTIGATION OF INTERFACE SPECIES

W. Giurlani[1], A. Lavacchi[2], A. Giaccherini[1], A. Comparini[1], E. Piciollo[3], F. Di Benedetto[4,5], F. d'Acapito[6] and M. Innocenti[1,2]
[1] Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3, 50019, Sesto Fiorentino (FI), Italy
[2] CNR, Istituto dei Composti Organometallici, via Madonna del Piano 10, 50019, Sesto Fiorentino (FI), Italy
[3] LEM Galvanica, Italy
[4] CNR, Istituto di Geoscienze e Georisorse, via G. La Pira, 4, 50121, Firenze, Italy
[5] Dipartimento di Scienze della Terra, Università di Firenze, via La Pira 4, 50121, Firenze (Italy).
[6] CNR, Istituto di Officina dei Materiali, OGG, c/o ESRF, Grenoble, France

Fuel cells are gradually taking place worldwide in the energetic panorama. These devices need to be understood in depth to improve the extrinsic energy efficiency; for this reason, an innovative analytical technique, focused on the reactions of the electrodic surface for heterogeneous catalytic reactions, has been developed. This technique is called FEXRAV (Fixed Energy X-ray Absorption Voltammetry) and represents an innovative, fast and easy[1] method for the in situ and in operando X-ray absorption analysis. The measurement is taken at LISA Beamline, in the synchrotron of Grenoble, recording the changes in X-ray absorption and/or fluorescence intensity while the electrode potential varies at a fixed of energy. In this way, it is possible to perform conventional electrochemical methods, like cyclic voltammetry, and follow the transition between different valence states of the elements under observation at the same time[2]. The in operando study allows to point out intermediate oxidation states and adsorption species that are not visible in an ordinary cyclic voltammetry; from these information it is also possible to extrapolate an hypothesis about the reaction mechanism. Palladium nanoparticles supported on carbon have been studied in solution of KOH, EtOH and $HCOO^-$ between 0V and 1.2V vs RHE at two different wavelengths. By results, it is possible to detect and quantify the percentage of oxide on the catalyst, the maximum overpotential that a full cell should reach before the poisoning of the catalyst and its loss in function of time; different trends have been recorded in different solutions, suggesting that different reaction mechanisms were taking place.

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CRITICAL ASSESMENT OF STRUCTURE AND COMPOSITION FOR NEW SEMICONDUCTIONG MATERIALS

A. De Luca[1], A. Giaccherini[1], A. Comparini, B. Pasquini[1], R.A. Picca[2], N. Cioffi[2], E. Piciollo[3], S. Furlanetto[1], F. Di Benedetto[4] and M. Innocenti[1]
[1] Dipartimento di Chimica, Università Degli Studi di Firenze, Firenze
[2] Dipartimento di Chimica, Università Degli Studi di Bari "Aldo Moro", Bari
[3] LEM galvanica, Italy
[4] Dipartimento di Scienze della Terra, Università Degli Studi di Firenze, Firenze

Silicon-based photovoltaic is a mature technology with very well established production process at an industrial scale. Efficiency and "Energy Return On Energy Investment" (EROEI) are minor concerns for devices base on doped crystalline silicon for the energy conversion [1]. On the contrary, decommissioning is a major concern due to silicon related pathologies. Moreover, the European Union release of an official list of critical raw materials that must be replaced or at least saved to secure future supply [2]. On this ground new materials for energy conversion should have very favourable Full Life Cycle Assessment (FLCA). Thus, sulphides containing very available metals, are among the most promising materials for the application in photovoltaics devices. Recently, new synthetic strategies for sulphides of Fe, Zn, Cu and Sn has been proposed. These materials are very interesting from the sustainability standpoint, the elements involved are very abundant, non-toxic and they ensure in some case high conversion efficiency (up to 12%). The process from the precursor to the photovoltaic cell involves a complex sequence of steps even at a laboratory scale. Our research aims to develop easier and more sustainable synthetic strategy for Kesterite type sulphides. In the field of the synthesis for material science, it is crucial to perform a critical assessment of the materials proprieties in order to reveal their relationship with the synthetic pathway. Clarifying these aspects of the synthesis it is a mandatory step in order to optimize the synthetic process. A characterization of these materials has been carried by means of CV, UV-VIS, XPS, SEM-EDX and XRD.

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STRONG ANIONIC RESIN CHARGED WITH SUPHOAZODYE FOR SENSING OF Pd, Cu AND Ni FROM AQUEOUS SOLUTION.

R. Biesuz, M. Pesavento, C. Giobbio, M. Vanzulli, G. Alberti
Dipartimento di Chimica, Università degli Studi di Pavia, Via Taramelli, 12 – 27100 Pavia

The presence of metal ions signalled by a colour change of solid phase is one of the most used strategy in metals sensing.
Here the preliminary results obtained sorbing 2-(tetrazolylazo)-l,8 dihydroxy naphthalene- 3,6,-disulphonic acid, named TazoC, on a Macroporous Strong Anion Exchange Resin, Marathon-Dow Chemical-USA for the simultaneous detection of Pd(II), Ni(II) and Cu(II) are presented.
The original idea was to develop a sensor for Palladium(II). Its affinity towards TazoC and similar ligands was known: the dye was synthetized in the past by our group and already used, in solution and also in the solid phase, but never before for the direct sensing of metals.
In figure 1- a, b and c- the colour of the solid phase, now named Mthn-TazoC, without any metal, i.e the colour of the free ligand at pH 4.5, is shown on the left, and compared on the right with the colour of the same solid after metal sorption.

a) Palladium b) Copper c) Nickel
Fig.1 Marathon resin with TazoC at pH 4.5, see text for details.

The azodye is sorbed very quickly by simple ion exchange on the solid.
As first task, a single metal calibration was undertaken through analysis of spectra of the solid phase obtained introducing the Mthn-TazoC resin, suspended in the aqueous phase, in 0.5 cm cuvette, vs a blank of the same resin not contacted with the metal ion.
The spectra are rather scattered particularly at low λ (below 450 nm), possibly because of non homogeneous cell packing (average signal of two different spectra on both side of the cuvette were collected), but mainly for the high absorptivity. The determination of the LOD, LOQ and the linear and dynamic ranges was the prelaminar step. For this purpose, the multivariate regression PLS, (Partial Least Square Regression) was applied. Compared to the classical univariate approach, by PLS the entire spectrum between 450 and 800 nm was used overcoming the problems of measuring only at λ of the complex maximum. Additionally, a multivariate regression becomes essential to develop calibration models for the simultaneous analysis of the three cations. The validity of the PLS models for Pd(II), Ni(II) and Cu(II) was verified analysing synthetic solutions, containing different quantity of the cations, and real spiked samples.

MODIFYING CONVENTIONAL UV-VIS CUVETTES WITH METALLIC/POLYMERIC COMPOSITE NANOMATERIALS FOR LOCALIZED SURFACE PLASMON RESONANCE (LSPR) ANALYSES FOR CULTURAL HERITAGE DIAGNOSIS

S. Scarano, C. Berlangieri, E. Carretti, L. Dei, P. Baglioni, and M. Minunni
Department of Chemistry 'Ugo Schiff' and CSGI, University of Florence, via della Lastruccia 3-13, Sesto Fiorentino, 50019, Firenze, Italy.

Localized Surface Plasmon Resonance (LSPR)-based biosensing is rapidly growing thanks to the huge possibilities in metallic and semi-metallic nanoparticles synthesis and their commercial availability, coupled to the facile and miniaturizable optical asset required to interrogate the plasmonic properties of these nanomaterials by transmission mode (1). In fact, LSPR of metal nanoparticles is easily observed by measuring changes in their extinction spectrum, both in terms of wavelength shift and absorbance intensity.
The near field elicited strongly depends on the figure of merit of the employed nanomaterial, i.e. metal type, size and aspect ratio of nanoparticles (NPs), their spatial distribution and the surrounding environment, with improved performances in sensitivity and selectivity than traditional SPR. Recently, starting from the observation that spontaneous reduction of Au(III) ions is obtainable by simple immersion of cured PDMS films into metal salt solutions, some paper dealing with the fabrication of these composite substrates for (bio)sensing purposes have appeared (1-7), also integrated to microfluidic design (6). Moreover, PDMS combines its excellent optical features in the visible range to the advantages of microfabrication. In this work we present the development of a simple and ease approach to revisit the use of traditional (quartz and/or plastic) UV-Vis cuvettes through their modification with metallic NPs/PDMS composites for combined LSPR/UV-Vis measurements. Gold NPs are grown on PDMS films, then the obtained composite nanomaterial has been modified with specific antibodies. As proof of concept, here anti-ovalbumin and anti-IgY were preliminary exploited as specific receptors for egg albumen and yolk detection, respectively, in the perspective of applying the method to the diagnosis of artistic surfaces, as recently reported by our group on classic SPR (8). Different conditions for NPs/PDMS growth were tested to optimize the optical features of the plasmonic material. Bulk sensitivities of different substrates were defined, and LSPR read out was realized on a classic spectrophotometric platform, achieving a simple, cheap and highly versatile biosensing approach alternative to classical SPR.

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SURFACE PLASMON RESONANCE IMAGING BIOSENSING FOR THE DETECTION OF *STAPHYLOCOCCUS AUREUS* IN FOOD

A. M. Aura[1], R. D'Agata[2], G. Spoto[1,2]
[1] Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale Andrea Doria, 6 – 95125 Catania
[2] Consorzio I.N.B.B., Viale delle Medaglie d'Oro 305 – 00136 Roma.

Staphylococcus aureus (*S. aureus*) is one of the most popular pathogenic bacteria involved in food poisoning worldwide [1]. The pathogenicity is due to its virulence factors, invasive capacity and antibiotic resistance [2].
Staphylococcal foodborne poisoning is caused by the ingestion of food having Staphylococcal Enterotoxins (SEs) [3]. According to Commission Regulation (EC) No 1441/2007, SEs must not be detected in five independent food sample portions to be safe for human consumption [4]. SEA, SEB, SEC and SED are the most frequently enterotoxins found in foods, and SEA is the most commonly recovered from food poisoning outbreaks [5].
Optical biosensors have received remarkable interest for bacterial pathogen detection [6]. Surface Plasmon Resonance Imaging (SPRI)-based biosensors allow the high sensitive, real-time and label-free monitoring of biomolecular interactions [7].
In this communication, we describe the development of SPRI biosensors for the detection of SEA. In particular, specific antibodies have been used to detect very low concentrations (ng/mL) of the toxin, also in complex food matrices (i.e. milk). At the same time SPRI genosensing capabilities have been explored, through the in situ genomic DNA hybridation to peptide nucleic acid probes immobilized on SPRI sensor surface. SPRI biosensor sensitivity benefited of the use of properly functionalized gold nanoparticles.

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ZnO NANOPARTICLES AS ANTIMICROBIAL AGENTS: GREEN ELECTROCHEMICAL PREPARATION AND ANALYTICAL CHARACTERIZATION

R.A. Picca[1], M.C. Sportelli[1], V. Villone[1], R. Lopetuso[1], N. Cioffi[1]
[1] Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via E. Orabona, 4 – 70126 Bari

ZnO nanomaterials are generally proposed as efficient antimicrobial agents [1]. Moreover, they are considered highly stable and compatible, exerting a low degree of toxicity towards humans. Their preparation can be achieved by hydrothermal methods, sol-gel or physical approaches, all of them suffering of some drawbacks (e.g. high costs, long time, poor yield, etc.). Electrochemical techniques may offer an alternative way based on green processes with high efficiency [2]. Following our previous work on the aqueous preparation of ZnO nanoparticles (NPs) stabilized by an anionic capping agent (sodium polystyrene sulfonate, PSS) [3], here we present how this process was scaled up improving its yield up to 0.1 g/h. Moreover, results about a parallel study carried out using cationic stabilizers (belonging to the class of Quaternary Ammonium Salts, QAS) will be also shown. In this case, the ultimate goal is the preparation of more efficient nanoantimicrobials by combining ZnONPs and QAS bioactivities. Data about the synthesis process will be correlated to the results of morphological (TEM) and spectroscopic (XPS, FTIR) characterizations performed on the NPs. In perspective, the developed nanomaterials will be employed to confer antimicrobial properties to industrial products (e.g. textiles).

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X-RAY PHOTOELECTRON SPECTROSCOPY AS A NEW TOOL TO STUDY THE INTERACTION BETWEEN CELLS AND INORGANIC NANOPARTICLES

S. Rella[1], A. Turco[1], S. Corvaglia[2], M. Moglianetti[2], P.P. Pompa[2], C. Malitesta[1]
[1]Laboratorio di Chimica Analitica, Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali (DiSTeBA), Università del Salento, Lecce – Italy
[2]Istituto Italiano di Tecnologia, Center for Biomolecular Nanotechnologies, Arnesano, Lecce – Italy

In recent years, nanomaterials have attracted huge interest for their potential use in nanomedicine as multifunctional carriers for drug delivery.
The continuous development of drug delivery systems (DDSs) has been extensively researched based on the need to maximize therapeutic efficacy while minimizing undesirable side effects. In particular, nanoparticles have received great attention as drug delivery carriers due to their unique properties.[1] NPs have a relatively large (functional) surface which is able to bind, adsorb and carry other compounds such as drugs, probes and proteins. The composition of the engineered nanoparticles may vary: functionalized metal nanoparticles, polymer, carbon and silica .[2]
Nanoparticle-based DDSs offer many advantages but there are still many limitations to be solved, such as poor drug loading, too rapid release (i.e., burst release), inadequate tissue distribution, and toxicity [1].
For these reasons it is most important to study the interaction between cell-nanoparticles to understand the internalization of NPs on cell cultures and to determine the toxicity. Many techniques (i.e. TEM, ICP, Confocal Microscopy) are used to characterize these samples but none of them give the possibility to understand if surface modification of NPs oxidation state can occur during cellular uptake/release, that can be indicative of their toxicity. In this work, we report a preliminary XPS study of inorganic nanoparticles to be used as candidates for drug delivery platforms. In particular, the combination of surface analysis technique with a method of removing the outer surface of a sample (sputtering) allowed us to have information about internalization of nanoparticles, to analyse multiple cells simultaneously and to identify the oxidation state of elements to have information about toxicity

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NANOPARTICLES-ENHANCED LASER-ABLATION ICP-MS OF METALLIC SAMPLES

F. Mastrorocco[1], L.C. Giannossa[2], C. Koral[1], A. De Giacomo[1], A. Mangone[1]
[1]Department of Chemistry, University of Bari, Via Orabona 4, Bari (Italy)
[2]Department of Economics, Management and Business Law University of Bari Aldo Moro, Largo Abbazia Santa Scolastica n. 53, 70124 Bari (Italy)

This research shows a preliminary study of nanoparticles-enhanced LA-ICP-MS, which aims to obtain an analytical procedure in order to improve the analytical performance of the technique in terms of sensitivity and LOD, without any changes in the experimental configuration. The undoubted strength of this approach is represented by its simplicity, affordability and fast performance. Laser parameters or the type and flow of gas carrier can be changed to improve the ablation of the sample. Otherwise, the sample can be altered in order to increase its response to laser, preserving its chemical properties.
This second method has been used, and in particular some drops of AuNPs colloidal dispersion were deposited on the sample's surface, and the solvent evaporated before it had been ablated. A remarkable increase in the measured signal intensity is observed due to the presence of nanoparticles. In analogy of what has already proved with Laser Induced Breakdown Spectroscopy [1,2], when a critical number of NPs are deposited on the target surface, the laser pulse electromagnetic field induces the collective oscillation of the conduction electrons of the NPs that in turn results in a strong enhancement of the field. The latter allows to switch the seed electron production in the ablation process from multiphoton ionization to electron field emission. In this frame a more efficient and homogeneous ablation can be obtained. In this work preliminary results of this approach during LA-ICP-MS of metallic alloys are shown and discussed with a systematic comparison of conventional LA-ICP-MS and nanoparticle enhanced LA-ICP-MS.

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QUALITY BY DESIGN AND CAPILLARY ELECTROPHORESIS IN THE DEVELOPMENT OF THYMOQUINONE-LOADED VESICULAR SYSTEMS FOR TOPICAL TREATMENT OF VITILIGO

B. Pasquini[1], N. Mennini[1], S. Orlandini[1], C. Caprini[1], P. Mura[1], M. Del Bubba[2], S. Furlanetto[1]
Dipartimento di Chimica "U. Schiff", Università degli Studi di Firenze, [1]Via U. Schiff 6 – [2]Via Della Lastruccia 3 – 50019 Sesto Fiorentino, Firenze

Vitiligo is a hypopigmentation disorder caused by the loss of melanocyte activity for melanin pigment generation. Recent studies have demonstrated that thymoquinone (TQ), a natural bio-active compound extracted from the seeds of *Nigella Sativa*, produces melanin stimulatory effects leading to skin darkening. A new and innovative vesicular formulation has been optimized for the topical treatment of vitiligo using Quality by Design (QbD) principles. Critical quality attributes were represented by vesicles size (size), polydispersity index (PDI) and encapsulation efficiency of TQ (EE%). Size and PDI were measured using dynamic light scattering, while EE% was determined with indirect method analyzing the free TQ by a fast capillary electrophoresis method. QbD scouting phase has made it possible to select the formulation components, to classify factors in different categories (formulation, process, method, environment) and to select the critical process parameters to be further studied by experimental design. Ethosomes composed of phospholipid, ethanol and water resulted the suitable vesicular carriers for topical delivery of TQ. Experimental design was efficiently used for rapid and systematic product development. A first screening phase was followed by response surface methodology. The contour plots were drawn and the design space (DS) was defined. The DS was visualized by means of probability maps and included all the operative conditions which led to fulfill the requirements of the quality product with a degree of probability $\pi \geq 90\%$. Experimental results, applying working point conditions, highlighted the good predictivity of the model and *ex vivo* studies performed by Franz diffusion cells confirmed that the TQ-loaded ethosomal system improved the penetration of the active compound into the skin.

A RAPID AND SIMPLE METHOD FOR THE ASSAY OF POLYAMINES IN HUMAN URINE BY SOLID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-TRIPLE QUADRUPOLE MASS SPECTROMETRY

R. Elliani[1], A. Naccarato[2], B. Cavaliere[1], G. Sindona[1], A. Tagarelli[1]
[1]Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via Pietro Bucci, Cubo 12/C – 87030 Arcavacata di Rende (CS)
[2]CNR-Istituto sull'Inquinamento Atmosferico, Divisione di Rende, Università della Calabria-Polifunzionale - 87036 Arcavacata di Rende (CS)

Over the last years, monitoring of low molecular weight biomarkers in biological fluids is having increasing importance related to the possible effects on the human health. Polyamines are aliphatic amines with low molecular weight, which are essential for normal growth and cellular differentiation. The marked increase of the biosynthesis of polyamines has been associated with rapid tumor growth, resulting in the increase of their levels in urine. Due to these findings, it is widely accepted that the polyamines are one of the most important cancer biomarkers for early diagnosis and treatment [1]. Major polyamines in cells are putrescine, cadaverine, spermidine and spermine, which are found in almost all living organism. Moreover, polyamines can exist as conjugate forms in cells and biofluids, in particular as acetylated forms. These compounds including N-acetylputrescine, N-acetylspermine and N-acetylspermidine.
The goal of the present work was the development of a fast and simple method for the quantification of these polyamines in human urine. The method provided aqueous derivatization based on alkyl chloroformate [2,3], followed by solid phase microextraction-gas chromatography-triple quadrupole mass spectrometry (SPME-GC-QqQ-MS) analysis. The signals were recorded in selected reaction monitoring (SRM) acquisition mode that allows the achievement of high specificity by selecting appropriate precursor–product ion couples. The derivatization reaction was directly carried out in urine with propyl chloroformate in order to obtain a fast and simple protocol. The extraction ability of five commercially available SPME fibers was evaluated in univariate mode, while the variables affecting the SPME analysis were optimized by the multivariate approach of "Experimental design" (DoE).

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