



UNIVERSITÀ  
DEGLI STUDI DI BARI  
ALDO MORO



## Incontro di Spettroscopia Analitica

*Matera 29 maggio - 1 giugno 2016*

# Book of Abstracts

## **Comitato Scientifico**

**Giuseppe Spoto**

*Università degli Studi di Catania*

**Marco Grotti**

*Università degli Studi di Genova*

**Luigia Sabbatini**

*Università degli Studi di Bari "Aldo Moro"*

**Anna Maria Salvi**

*Università degli Studi della Basilicata*

## **Comitato Organizzatore**

### **Università degli Studi di Bari "Aldo Moro"**

Luigia Sabbatini

Nicola Cioffi

Elvira De Giglio

Nicoletta Ditaranto

Rosaria Anna Picca

Inez D. van der Werf

### **Università degli Studi della Basilicata**

Anna Maria Salvi

Rosanna Ciriello

Maria Elvira Carbone

Michela Contursi

Fausto Langerame

Licia Viggiani

## **Premio Mazzucotelli**

*In occasione dell'Incontro di Spettroscopia Analitica (ISA), il Gruppo di Spettroscopia Analitica (GSA), appartenente alla Divisione di Chimica Analitica della Società Chimica Italiana, conferisce il Premio intitolato al Prof. Ambrogio Mazzucotelli, prematuramente scomparso e già aderente al Gruppo, attraverso il quale ha operato per promuovere e valorizzare le ricerche in questo settore della chimica analitica.*

*Il Premio viene assegnato con cadenza biennale a giovani studiosi la cui attività di ricerca nel campo della Spettroscopia Analitica risalti particolarmente sia per l'originalità e qualità dei metodi che per la rilevanza dei risultati.*



# PROGRAMMA ISA 2016

Lunedì 30 Maggio

8:30 - 9:45 Registrazione

9:45 - 10:30 Inaugurazione del Congresso

*Saluti di benvenuto*

*Commemorazione Prof. Pier Giorgio Zambonin (Elio Desimoni, Università di Milano)*

**Chairperson: Prof. Nicola Cioffi**

**10:30 - 11:10** **Main Lecture:** Boris Mizaikoff  
*Institute of Analytical and Bioanalytical Chemistry, University of ULM, Germany*  
***Miniaturization in Mid-Infrared Sensor Technology: Is Small Also Useful?***

11:10- 11:50 Pausa caffè, Registrazione

**Chairperson: Prof. Giuseppe Spoto**

11.50-12.10 ***New developments in Quartz enhanced photoacoustic gas sensing in the Infrared and THz spectral ranges***  
V. Spagnolo<sup>1</sup>, P. Patimisco<sup>1,2</sup>, A. Sampaolo<sup>1,2</sup>, M. Giglio<sup>1</sup>, G. Scamarcio<sup>1</sup>, Frank K. Tittel<sup>2</sup>  
<sup>1</sup> Dipartimento Interateneo di Fisica, Università degli Studi di Bari e Politecnico di Bari  
<sup>2</sup> Department of Electrical and Computer Engineering, Rice University – USA

12.10-12.30 ***Detection of foodborne pathogens by optical biosensing***  
A. M. Aura<sup>1</sup>, R. D'Agata<sup>2</sup>, G. Spoto<sup>1,2</sup>  
<sup>1</sup>Dipartimento di Scienze Chimiche, Università di Catania  
<sup>2</sup>Consorzio I.N.B.B. Roma

12.30-12.50 ***Spectroscopic and morphological characterization of antibacterial properties of Ag-fluoropolymer thin films by AFM and IR-ATR spectroscopy***  
M. C. Sportelli<sup>1</sup>, E. Tütüncü<sup>2</sup>, R. A. Picca<sup>1</sup>, M. Valentini<sup>3</sup>, A. Valentini<sup>3</sup>, C. Kranz<sup>2</sup>, B. Mizaikoff<sup>2</sup>, N. Cioffi<sup>1</sup>  
<sup>1</sup>Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro"  
<sup>2</sup>Institute of Analytical and Bioanalytical Chemistry, Ulm University – Germany  
<sup>3</sup>Dipartimento Interateneo di Fisica "M. Merlin"

12:50 - 13:50 Pausa pranzo

**Chairperson: Prof.ssa Anna Maria Salvi**

**13.50-14.30** **Main Lecture:** Andreas Thissen  
*SPECS Surface Nano Analysis GmbH, Germany*  
***EnviroESCA-The Beginning of a New Era***

14.30-14.50 **Assessment of corrosion inhibition by X-Ray Photoelectron Spectroscopy and Electrochemical Impedance Spectroscopy**

M. P. Casaletto, V. Figà

*Istituto per lo Studio dei Materiali Nanostrutturati – Consiglio Nazionale delle Ricerche*

14.50-15.10 **Purple photosynthetic bacteria and sea urchin coelomocytes examination by X-ray photoelectron spectroscopy as a non-conventional analytical technique for bio-organic materials**

M. R. Guascito<sup>1,2</sup>, L. Giotta<sup>1</sup>, P. Pagliara<sup>1</sup>, D. Chirizzi<sup>2</sup>, S. Rella<sup>1</sup>, D. Mastrogiacomo<sup>1</sup>, F. Milano<sup>3</sup>

<sup>1</sup>*Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento*

<sup>2</sup>*Istituto di Scienze dell'Atmosfera e del Clima, ISAC-CNR, Lecce*

<sup>3</sup>*Istituto per i Processi Chimico Fisici, UOS Bari*

15.10-15.30 **Electrosynthesis, spectroscopic characterization and biological evaluation of Gallium- or Silver- modified chitosan coatings on titanium implants**

M. A. Bonifacio<sup>1</sup>, S. Cometa<sup>2</sup>, M. M. Giangregorio<sup>3</sup>, M. Dicarolo<sup>4</sup>, M. Mattioli-Belmonte<sup>4</sup>, L. Sabbatini<sup>1</sup>, E. De Giglio<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Bari "Aldo Moro"*

<sup>2</sup>*Jaber Innovation srl*

<sup>3</sup>*Nanotec-CNR, Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro"*

<sup>4</sup>*Department of Clinical and Molecular Sciences, Università Politecnica delle Marche*

**15.30 – 17.00 Sessione poster e Pausa caffè**

**Chairperson: Prof.ssa Antonella Rossi**

17.00-17.20 **Silicon nanowires: synthesis, structural properties and photonic applications**

C. D'andrea<sup>1</sup>, M.J. Lo Faro<sup>1,2,3</sup>, B. Fazio<sup>2</sup>, P. Musumeci<sup>3</sup>, S. Trusso<sup>2</sup>, P.M. Ossi<sup>4</sup>, F. Neri<sup>5</sup>, G. Franzò<sup>1</sup>, F. Iacona<sup>1</sup>, F. Priolo<sup>1,3,6</sup>, A. Irrera<sup>2</sup>

<sup>1</sup>*MATIS CNR-IMM, Istituto per la Microelettronica e Microsistemi, Catania*

<sup>2</sup>*CNR-IPCF, Istituto per i Processi Chimico-Fisici, Messina*

<sup>3</sup>*Dipartimento di Fisica ed Astronomia, Università di Catania*

<sup>4</sup>*Dipartimento di Energia & Centre for Nano Engineered Materials and Surfaces, NEMAS Politecnico di Milano*

<sup>5</sup>*Dipartimento di Fisica e di Scienze della Terra, Università di Messina*

<sup>6</sup>*Scuola Superiore di Catania*

17.20-17.40 **Nanoparticles Enhanced Laser Induced Breakdown Spectroscopy: concepts and applications and perspectives**

A. De Giacomo<sup>1,2</sup>, M. Dell'Aglio<sup>2</sup>, R. Gaudioso<sup>1,2</sup>, C. Koral<sup>1</sup>, G. Valenza<sup>1,2</sup>

<sup>1</sup>*Dipartimento di Chimica, Università di Bari*

<sup>2</sup>*CNR-NANOTEC, Bari*

17.40-18.00 **X-Ray Photoelectron Spectroscopy as a new tool to study cell uptake of inorganic nanoparticles**

S. Rella<sup>1</sup>, A. Turco<sup>1</sup>, S. Corvaglia<sup>2</sup>, M. Moglianetti<sup>2</sup>, P. P. Pompa<sup>2</sup>, C. Malitesta<sup>1</sup>

<sup>1</sup>*Dipartimento di Scienze e Tecnologie Biologiche e Ambientali (DiSTeBA), Università del Salento*

<sup>2</sup>*Istituto Italiano di Tecnologia, Center for Biomolecular Nanotechnologies, Lecce*

**18.00-18.30 Comunicazione degli Sponsor**

**Single particle ICP-MS for nanoparticle analysis in various matrixes**

A. Piron (Product Specialist Inorganic PerkinElmer)

**18:30 – Visita alla mostra "Leonardo da Vinci nei Sassi di Matera"**

## Martedì 31 Maggio

### Chairperson: Prof. Nicola Cioffi

**09:00 - 9:40** **Main Lecture:** Christine Kranz, D. Neubauer, J. Izquierdo, B. Mizaikoff  
*Institute of Analytical and Bioanalytical Chemistry, University of ULM, Germany*  
**Combined Scanning Probe Microscopy with Mid-IR Spectroelectrochemistry**

**09:40 - 10:10** **Premio Mazzucotelli (ex aequo) – Filippo Mangolini**  
*Institute of Functional Surfaces, School of Mechanical Engineering, University of Leeds, UK*  
**Quantitative Evaluation of the Carbon Hybridization State by Near Edge X-ray Absorption Fine Structure Spectroscopy**

**10:10 - 11:40** Sessione poster - Pausa caffè - Registrazione

### Chairperson: Dott. Alessandro d'Ulivo

**11.40-12.00** **Human exposure to thallium through tap water: a study from Valdicastello Carducci and Pietrasanta (northern Tuscany, Italy)**  
B. Campanella<sup>1,2</sup>, M. Onor<sup>1</sup>, A. D'Ulivo<sup>1</sup>, R. Giannecchini<sup>3</sup>, M. D'Orazio<sup>3</sup>, R. Petri<sup>3</sup>, E. Bramanti<sup>1</sup>  
<sup>1</sup>C.N.R Istituto di Chimica dei Composti Organometallici, UOS di Pisa  
<sup>2</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa  
<sup>3</sup>Dipartimento di Scienze della Terra, Università di Pisa

**12.00-12.20** **Spectroscopic analyses of foods with a low environmental impact**  
M. Innocenti<sup>1</sup>, M. L. Meloni<sup>1</sup>, S. Bellassai<sup>2</sup>, S. Pucci<sup>2</sup>, P. Giusti<sup>2</sup>, S. Orlandini<sup>1</sup>, S. Furlanetto<sup>1</sup>  
<sup>1</sup>Dipartimento di Chimica, Università di Firenze  
<sup>2</sup>CDR srl, Firenze

**12.20-12.40** **Combined biological assays and X-ray spectroscopy techniques to assess the bioavailability of arsenic in two industrial contaminated soils**  
I. Allegretta\*, C. Porfido, O. Panzarino, R. Terzano, E. de Lillo, M. Spagnuolo  
*Dipartimento di Scienze del Suolo, della Pianta e degli Alimenti, Università degli Studi di Bari "Aldo Moro"*

**12.40-13.00** **Determination Of Total And Free Cyanide In Soil By Isotope Dilution GC/MS Following Pentafluorobenzyl Derivatization**  
B. Campanella<sup>1,2</sup>, L. Biancalana<sup>1</sup>, M. Onor<sup>2</sup>, E. Bramanti<sup>2</sup>, A. D'Ulivo<sup>2</sup>, Z. Mester<sup>3</sup>, E. Pagliano<sup>3</sup>  
<sup>1</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa  
<sup>2</sup>Consiglio Nazionale delle Ricerche (CNR), Istituto di Chimica dei Composti Organometallici, UOS di Pisa  
<sup>3</sup>National Research Council of Canada

**13:00 - 14:00** Pausa pranzo

**Chairperson: Prof. Rocco Mazzeo**

- 14.00-14.30 **Keynote Lecture:** A. Andreotti<sup>1</sup>, S. Vettori<sup>2</sup>, B. Sacchi<sup>2</sup>, P. Tiano<sup>2</sup>, L. Rampazzi<sup>3</sup>, M. P. Colombini<sup>2</sup>  
<sup>1</sup>Department of Chemistry and Industrial Chemistry, University of Pisa  
<sup>2</sup>Institute for the Conservation and Valorization of Cultural Heritage, CNR Sesto Fiorentino  
<sup>3</sup>Università degli Studi dell'Insubria  
**An analytical study for the conservation of the Matera Cathedral**
- 14.30-14.50 **Calibration-Free quantitative analysis of Antoninianus coins by Laser-Induced Breakdown Spectroscopy (LIBS) in depth-profile mode**  
R. Gaudiuso<sup>1,2</sup>, L. C. Giannossa<sup>1</sup>, A. Mangone<sup>1</sup>, O. De Pascale<sup>2</sup>, A. De Giacomo<sup>1,2</sup>  
<sup>1</sup>Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro"  
<sup>2</sup>Nanotec (Institute of Nanotechnology) – CNR Bari
- 14.50-15.10 **Characterization of zinc carboxylates in modern paintings at the macro and micro-scale by FTIR spectroscopy**  
F. Rosi<sup>1</sup>, F. Gabrieli<sup>1</sup>, L. Cartechini<sup>1</sup>, A. Vichi<sup>2</sup>, S. G. Kazarian<sup>2</sup>, C. Miliani<sup>1</sup>  
<sup>1</sup>CNR-ISTM, Istituto di Scienze e Tecnologie Molecolari, Perugia  
<sup>2</sup>Department of Chemical Engineering, Imperial College London, UK
- 15.10-15.30 **Spectroscopic Studies Of Medieval Wall Paintings Of Salento (Puglia, Italy): Characterisation Of Pigment And Techniques**  
D. Fico, A. Pennetta, G. E. De Benedetto  
Laboratorio di Analisi Chimiche per l'Ambiente ed i Beni Culturali, Università del Salento

**15:30 - 16:50 Sessione poster e Pausa caffè**

**Chairperson: Prof.ssa Luigia Sabbatini**

- 16.50-17.10 **An advanced FTIR method for the analyses of dyes micro-extracts**  
S. Prati<sup>1</sup>, M. Milosevic<sup>2</sup>, G. Sciutto<sup>1</sup>, I. Bonacini<sup>1</sup>, S. G. Kazarian<sup>3</sup>, R. Mazzeo<sup>1</sup>  
<sup>1</sup>Dipartimento di Chimica, Università di Bologna  
<sup>2</sup>MeV Technologies LLC, USA  
<sup>3</sup>Department of Chemical Engineering, Imperial College London, UK
- 17.10-17.30 **Non-invasive spectroscopic techniques for the diagnosis of Saint Francis's Chartula, before and after the consolidation treatments based on CaCO<sub>3</sub> nanoparticles**  
F. Valentini<sup>1</sup>, M. Bicchieri<sup>2</sup>  
<sup>1</sup>Dipartimento di Chimica, Università di Tor Vergata  
<sup>2</sup>Istituto Centrale per il Restauro e la Conservazione del Patrimonio Archivistico e Librario, Roma
- 17.30-17.50 **Iron stains on carbonate artefacts: XPS investigation of corrosion-induced deterioration on reference stones**  
F. Langerame<sup>1</sup>, T. Lovaglio<sup>2</sup>, R. Reale<sup>3</sup>, A. M. Salvi<sup>1</sup>, M. P. Sammartino<sup>3</sup>, Gi. Visco<sup>3</sup>  
<sup>1</sup>Dipartimento di Scienze, Università degli Studi della Basilicata  
<sup>2</sup>Scuola di Scienze Agrarie, Forestali, Alimentari e Ambientali, Università della Basilicata,  
<sup>3</sup>Dipartimento di Chimica, Università degli Studi 'La Sapienza'

**17.50-18.30 Assemblea Gruppo**

**20:00 Cena Sociale - Premiazione "miglior poster"**

## Mercoledì 1 Giugno

Chairperson: Prof. Sabino A. Bufo

- 09:00 - 9:30** **Premio Mazzucotelli (ex aequo) – F. Ardini**  
*Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova*  
**Inductively coupled plasma mass spectrometry as a powerful tool for the determination of arsenic and selenium species for environment, food and health**
- 9.30-9.50 **Interference-free detection of SiO<sub>2</sub> nanoparticles in marketed food samples by AF4-ICP-MS/MS**  
F. Aureli<sup>1</sup>, L. Bellarosa<sup>1,2</sup>, M. D'Amato<sup>1</sup>, C. Mucchino<sup>2</sup>, A. Raggi<sup>1</sup>, F. Cubadda<sup>1</sup>  
<sup>1</sup>Department of Food Safety, Nutrition and Veterinary Public Health, Istituto Superiore di Sanità, Rome  
<sup>2</sup>Dipartimento di Chimica, Università degli studi di Parma
- 9.50-10.10 **Targeted and untargeted alkaloids profiling of alpine flora using high resolution mass spectrometry (Q-Orbitrap)**  
T. Nardin<sup>1</sup>, E. Piasentier<sup>2</sup>, C. Barnaba<sup>1</sup>, M. Malacarne<sup>1</sup>, R. Larcher<sup>1</sup>  
<sup>1</sup>Centro Trasferimento Tecnologico, Fondazione E. Mach, San Michele all'Adige (TN)  
<sup>2</sup>Dipartimento di scienze agrarie ed ambientali (DISA), Università di Udine
- 10.10-10.30 **Photocatalysis of Pollutants' degradation using TiO<sub>2</sub> Coated Glass**  
F. Lelario<sup>1</sup>, Samer Khalaf<sup>1</sup>, Monica Brienza<sup>1</sup>, Sabino A. Bufo<sup>1</sup>, Laura Scrano<sup>2</sup>  
<sup>1</sup>Dipartimento di Scienze, Università della Basilicata  
<sup>2</sup>DICEM), Università della Basilicata
- 10.30-10.50 **Bimetal Cu/Ag nanoparticles synthesized by laser ablation in aqueous and organic solution: process optimization and materials characterization**  
M.C. Sportelli<sup>1,2</sup>, A. Ancona<sup>1</sup>, R.A. Picca<sup>2</sup>, M. Izzi<sup>2</sup>, A. Di Maria<sup>2</sup>, A. Volpe<sup>1,3</sup>, P.M. Lugarà<sup>1,3</sup>, N. Cioffi<sup>2</sup>  
<sup>1</sup>Istituto di Fotonica e Nanotecnologie-CNR, Dipartimento Interateneo di Fisica "M. Merlin", Bari  
<sup>2</sup>Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro"  
<sup>3</sup>Dipartimento Interateneo di Fisica "M. Merlin", Università degli Studi di Bari "Aldo Moro"
- 10.50-11.10 **Characterization of brass alloys aged at open circuit potential in neutral solution**  
F. Cocco<sup>1</sup>, B. Elsener<sup>1,2</sup>, M. Fantauzzi<sup>1</sup>, S. Palomba<sup>1</sup>, A. Rossi<sup>1</sup>  
<sup>1</sup>Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari  
<sup>2</sup>ETH Zurich, Institute for Building Materials

**11:15 Chiusura del Congresso**

**Gita sociale ai SASSI con degustazione di prodotti tipici**



## ELENCO POSTER

- P1** **Untargeted high resolution mass analytical method (SPE-LC- Q-Orbitrap) for glycosylated simple phenol profiling in natural food matrices**  
Chiara Barnaba, Tiziana Nardin, Giorgio Nicolini, Roberto Larcher  
Centro Trasferimento Tecnologico, Fondazione E. Mach, San Michele all'Adige (TN)
- P2** **A surface plasmon resonance sensor based on molecularly imprinted polymer for transformer oil control**  
Maria Pesavento<sup>1</sup>, Nunzio Cennamo<sup>2</sup>, Luigi Zeni<sup>2</sup>, Simone Marchetti<sup>1</sup>, Antonella Profumo<sup>1</sup>, Daniele Merli<sup>1</sup>, Letizia De Maria<sup>3</sup>  
<sup>1</sup>Dipartimento di Chimica, Università di Pavia  
<sup>2</sup>Dipartimento di Ingegneria Industriale e Informatica, Seconda Università di Napoli  
<sup>3</sup>RSE research on Energetic System S.p.A. Milano
- P3** **Electrosynthesis and characterization of composite material platinum nanoparticles/polypyrrole nanowires for sensing applications**  
Antonio Caroli, Elisabetta Mazzotta, Simona Rella, Antonio Turco, Cosimino Malitesta  
Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento
- P4** **Spectroscopic and electrochemical characterization of Nickel-Cobalt/Graphene/Polyvinyl alcohol nanocomposites**  
Michela Contursi, Donatella Coviello, Innocenzo G. Casella  
Dipartimento di Scienze, Università degli Studi della Basilicata
- P5** **Fourier Transform Infrared Spectroscopy in the leather quality control: the project LIFETAN: and eco friendly tanning cycle**  
Emilia Bramanti<sup>1</sup>, Valentina Della Porta<sup>1</sup>, Massimo Onor<sup>1</sup>, Beatrice Campanella<sup>1,2</sup>, Alessandro D'Ulivo<sup>2</sup>, Emanuela Pitzalis<sup>1</sup>, Marco Carlo MAScherpa<sup>1</sup> and Alice Dall'Ara<sup>3</sup>  
<sup>1</sup>Consiglio Nazionale delle Ricerche (CNR), Istituto di Chimica dei Composti Organometallici, UOS di Pisa  
<sup>2</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa  
<sup>3</sup>Unità Tecnica Tecnologie dei Materiali Faenza (UTTMATF)
- P6** **Halloysite Nanotubes (HNTs) and Kaolinite (Kao): Fourier Transform Infrared Spectroscopy (FT-IR) study of the interactions with bovine serum albumin (BSA)**  
Valentina Della Porta<sup>1</sup>, Celia Duce<sup>2</sup>, Maria Rosaria Tinè<sup>2</sup>, Emilia Bramanti<sup>1</sup>  
<sup>1</sup>Consiglio Nazionale delle Ricerche (CNR), Istituto di Chimica dei Composti Organometallici, UOS di Pisa  
<sup>2</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa
- P7** **Loading of BSA,  $\alpha$ -Lac and  $\beta$ -Lg into Halloysite nanotubes: study of protein conformation by Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy and thermogravimetric analysis (TGA)**  
Valentina Della Porta<sup>1</sup>, Celia Duce<sup>2</sup>, Maria Rosaria Tinè<sup>2</sup>, Lisa Ghezzi<sup>2</sup>, Alessio Spepi<sup>2</sup>, Emilia Bramanti<sup>1</sup>  
<sup>1</sup>Consiglio Nazionale delle Ricerche (CNR), Istituto di Chimica dei Composti Organometallici, UOS di Pisa  
<sup>2</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa
- P8** **Combined LC-MS/MS and Molecular Networking approach to discover novel metabolites**  
Gerardo Della Sala  
NeaNat group, TheBlueChemistryLab, Dipartimento di Farmacia, Università degli Studi di Napoli "Federico II"
- P9** **A general approach to the immobilization of glyco-enzymes acting in cascade inside calcium alginate beads**  
Antonella Mallardi<sup>1</sup>, Valeria Angarano<sup>2</sup>, M. Magliulo<sup>2</sup>, L. Torsi<sup>2</sup>, Gerardo Palazzo<sup>2</sup>  
<sup>1</sup>CNR - IPCF, Istituto per i Processi Chimico-Fisici, Bari  
<sup>2</sup>Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro"
- P10** **XPS characterization of mussel adhesive protein inspired coatings: screening of optimal conditions for facile biomolecules conjugation**  
Simona Rella, Elisabetta Mazzotta, Antonio Turco, Antonio Caroli, Cosimino Malitesta  
Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali (Di.S.Te.B.A.), Università del Salento

- P11** **Characterization of new naturalised dyes by FTIR and atomic spectrometry**  
 Emilia Bramanti<sup>1</sup>, Marco Mascherpa<sup>1</sup>, Emanuela Pitzalis<sup>1</sup>, Massimo Onor<sup>1</sup>, Alessandro D'Ulivo<sup>1</sup>, M. Corsi<sup>2</sup>, M. Bonanni<sup>2</sup>, R. Bianchini<sup>2</sup>  
<sup>1</sup>C.N.R., Istituto di Chimica dei Composti Organo metallici, Sezione di Pisa  
<sup>2</sup>Dipartimento di Chimica 'Ugo Schiff', Università di Firenze
- P12** **Vapor generation for trace element determination. Focus on Cadmium**  
Emanuela Pitzalis, Davide Angelini, Marco Carlo Mascherpa, Alessandro D'Ulivo  
 C.N.R., Istituto di Chimica dei Composti Organo metallici, Sezione di Pisa
- P13** **Innovative natural defatting agents: FTIR study of the interaction with leather proteins and monitoring of the environmental impact**  
 Valentina Della Porta<sup>1</sup>, Massimo Corsi<sup>2</sup>, Roberto Bianchini<sup>2</sup>, Massimo Onor<sup>1</sup>, Emanuela Pitzalis<sup>1</sup>, Alessandro D'Ulivo<sup>1</sup>, Emilia Bramanti<sup>1</sup>  
<sup>1</sup>Consiglio Nazionale delle Ricerche (CNR), Istituto di Chimica dei Composti Organometallici, UOS di Pisa  
<sup>2</sup>Dipartimento di Chimica 'Ugo Schiff', Università di Firenze
- P14** **Characterization of sheep skin by FT-IR spectroscopy, after the degreasing stage with formulations containing lactose derivatives**  
 Valentina Della Porta<sup>1</sup>, Emilia Bramanti<sup>1</sup>, Massimo Corsi<sup>2</sup>, Marco Bonanni<sup>3</sup>, Roberto Bianchini<sup>2</sup>  
<sup>1</sup>Consiglio Nazionale delle Ricerche (CNR), Istituto di Chimica dei Composti Organometallici, UOS di Pisa  
<sup>2</sup>Dipartimento di Chimica 'Ugo Schiff', Università di Firenze  
<sup>3</sup>Glycolor srl
- P15** **UV-photochemical vapor generation at trace level of selenium species with a germicidal mercury lamp and low organic acid concentration**  
M. Onor<sup>1</sup>, A. Menciassi<sup>1</sup>, B. Campanella<sup>1,2</sup>, A. D'Ulivo<sup>1</sup>  
<sup>1</sup>Consiglio Nazionale delle Ricerche (CNR), Istituto di Chimica dei Composti Organometallici, UOS di Pisa  
<sup>2</sup>Dipartimento di Chimica e Chimica Industriale, Università di Pisa
- P16** **Investigation of industrial polyurethane foams modified by electrosynthesized copper nanoparticles**  
 Rosaria Anna Picca<sup>1</sup>, Maria Chiara Sportelli<sup>1</sup>, Ruggiero Quarto<sup>1</sup>, Antonio Valentini<sup>2</sup>, Nicola Cioffi<sup>1</sup>  
<sup>1</sup>Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro"  
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- Evaluation of the growth orientation of molecules in PoAP thin films:**
- P17**
  - **In situ electrochemical growth by AFM**
  - **Ar cluster ion etch profiles**
 Maria E. Carbone<sup>1</sup>, James E. Castle<sup>2</sup>, Rosanna Ciriello<sup>1</sup>, Anna M. Salvi<sup>1</sup>, Jon Treacy<sup>3</sup>, Peter Zhdan<sup>2</sup>  
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<sup>2</sup>Department of Mechanical Engineering Science, University of Surrey, Guildford, UK  
<sup>3</sup>Thermo Fisher Scientific, The Birches Industrial Estate, UK
- P18** **Electrochemically produced ZnO nanoparticles: synthesis in aqueous medium and morphological/spectroscopic characterization**  
Rosaria Anna Picca<sup>1</sup>, Maria Chiara Sportelli<sup>1</sup>, Riccarda Lopetuso<sup>1</sup>, Vincenzo Villone<sup>1</sup>, Nicola Cioffi<sup>1</sup>  
<sup>1</sup>Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro"
- P19** **A micro-invasive approach for the characterization of finishes on ancient monuments of Lecce (Puglia, Italy)**  
 Daniela Fico  
 Laboratorio di Analisi Chimiche per l'Ambiente ed i Beni Culturali, Università del Salento
- P20** **Titania based innovative nanocomposites to prevent stone artworks biodeterioration**  
 Nicoletta Ditaranto<sup>1,2</sup>, Rocco Guagnano<sup>1</sup>, Roberto Comparelli<sup>3</sup>, Luigia Sabbatini<sup>1,2</sup>  
<sup>1</sup>Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro"  
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<sup>3</sup>Istituto per i Processi Chimico-Fisici, CNR UOS Bari
- P21** **Characterisation of bioactive nanocomposites for stone conservation with VAR-FTIR spectroscopy**  
Inez Dorothé van der Werf<sup>1</sup>, Giulia Germinario<sup>1</sup>, Nicoletta Ditaranto<sup>1,2</sup>, Maria Chiara Sportelli<sup>1</sup>, Rosaria Anna Picca<sup>1</sup>, Luigia Sabbatini<sup>1,2</sup>  
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# Invited presentations

## Miniaturization in Mid-Infrared Sensor Technology: Is Small Also Useful?

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A wide variety of optical spectroscopy and sensing platforms nowadays benefit from miniaturization and system integration technologies ideally providing direct access to molecule-specific information. In-situ sensing strategies e.g., in harsh environments or for point-of-care diagnostics clearly become more prevalent, and label-free detection schemes additionally facilitate localized on-site analysis close to real-time.

However, decreasing the analytically probed volume may adversely affect the associated analytical figures of merit such as the signal-to-noise-ratio, the representativeness of the sample, or the fidelity of the obtained analytical signal. Consequently, the guiding paradigm for the miniaturization of optical diagnostics should entail chem/bio sensing platforms that are as small as still useful, rather than as small as possible smartly capitalizing on the advantageous features of integrated photonics.

Mid-infrared (MIR; 3-20  $\mu\text{m}$ ) sensor technology is increasingly adopted in environmental analysis, process monitoring and biodiagnostics due to the inherent molecular specificity enabling the discrimination of molecular constituents at ppm-ppb concentration levels in condensed and vapor phase media. Recently emerging strategies taking advantage of innovative waveguide technologies such as substrate-integrated hollow waveguides (gas phase sensing), and planar semiconductor waveguides (liquid phase sensing) in combination with highly efficient light sources including quantum cascade and interband cascade lasers (QCLs, ICLs) facilitate compact yet robust MIR diagnostic platforms for label-free chem/bio sensing and diagnostics.

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## **EnviroESCA – The Beginning of a New Era**

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Since many decades XPS (or ESCA) is the well-accepted standard method for non-destructive chemical analysis of solid surfaces. To fulfill this task existing ESCA tools combine reliable quantitative chemical analysis with comfortable sample handling concepts, integrated into fully automated compact designs. Over the last years it has been possible to develop XPS systems, that can work far beyond the standard conditions of high or ultrahigh vacuum. Near Ambient Pressure (NAP) XPS has become a fastly growing field in research inspiring many scientist to transfer the method to completely new fields of application. Thus, by crossing the pressure gap, new insights in complicated materials systems have become possible using either synchrotron radiation or laboratory X-ray monochromators as excitation sources under NAP condtions. Based on this experience SPECS Surface Nano Analysis GmbH has developed a revolutionary tool to realize the long existing dream in many analytical laboratories: reproducible chemical surface analysis under any environmental condition. EnviroESCA allows for different applications, like extremely fast solid surface analysis of degassing (but also non-degassing) samples, ESCA analysis of liquids or liquid-solid interfaces, chemical analysis of biological samples, materials and device analysis under working conditions (in situ/in operando studies of catalysts, electrochemical devices etc.). Discover the new capabilities of EnviroESCA, a fully automated tool in a new sophisticated and compact design with uncompromising ease-of-use, and explore completely new fields of applications for the established analysis method XPS.

## **Combined Scanning Probe Microscopy with Mid-IR Spectroelectrochemistry**

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The investigation of interfacial processes requires analytical techniques providing molecular selectivity, high sensitivity with the appropriate temporal/spatial resolution. Hence in recent years, effort was dedicated towards the development of hyphenated analytical platforms combining electrochemical and/or molecularly specific information with spatially resolved measurements. For example, molecular specific information along with topographical information of electrochemical processes can be obtained by combining IR spectroelectrochemistry using in-situ infrared attenuated total reflection spectroscopy (IR-ATR) with atomic force microscopy (AFM) [1] or in combination with scanning electrochemical microscopy (SECM) [2]. For spectroelectrochemical investigations in the mid-IR region boron-doped diamond (BDD) is highly suitable as transparent electrode. BDD is a metallic-like semiconductor providing a large potential window, chemical inertness, favorable signal-to-noise-ratio and a broad spectroscopic window ranging from the near UV to the far IR spectral regime. This superior chemical and physical properties [3] in combination and the possibility to fabricate BDD-modified diamond ATR crystals, renders BDD highly suitable for spectroelectrochemical applications. As examples of such combined measurements, the electrochemical deposition of conducting polymers was investigated via AFM and IR-ATR. AFM provides the advantages that additional information on e.g., adhesion forces can be determined. In order to improve the electrochemical sensitivity and to take advantage of the so-called surface enhanced infrared absorption (SEIRA), the BDD can be electrochemically modified with metal nanoparticles such as gold and silver nanoparticles (NPs) [4]. The present contribution gives an overview of the state-of-the-art of combining scanning probe techniques with mid-IR-ATR spectroscopy for in-situ (solution) investigations of processes occurring at the BDD or Au nanoparticle-modified BDD surface. This presentation will give an overview on the state-of-the-art, current challenges, and the future potential of combined analytical surface techniques.

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## Quantitative Evaluation of the Carbon Hybridization State by Near Edge X-ray Absorption Fine Structure Spectroscopy

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Carbon-based materials exist in a range of forms, including diamond, graphite, graphene, nanotubes, fullerenes, diamond-like carbon, carbides, polymers, and many other composites. The widespread use of carbon-based materials derives from their exceptional properties (*e.g.*, mechanical, electrical, and optical), which are in part due to the ability of carbon to hybridize in multiple bonding states (*i.e.*,  $sp^3$ ,  $sp^2$ , and  $sp$ ), and to strongly bind to many other elements, such as hydrogen. Due to the strong dependency of the aforementioned properties on the carbon hybridization states, the local ordering, and the degree of hydrogenation, the characterization of the structure of carbon-based materials is of paramount importance for engineering materials able to meet the performance and durability requirements of technologically-advanced applications, especially in harsh environments.

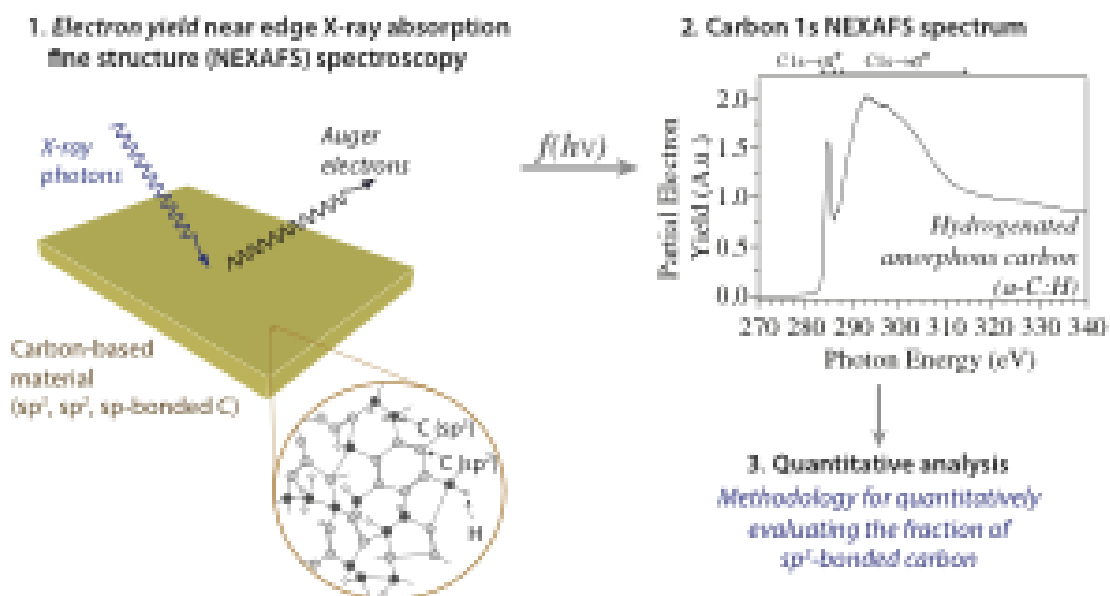
Among the several surface-analytical methods used to characterize carbon-based materials, carbon 1s near edge X-ray absorption fine structure (NEXAFS) spectroscopy is one of the most powerful techniques for gaining insights into the bonding configuration of near-surface carbon atoms, as demonstrated by its extensive use in the published literature. In spite of this, a critical assessment of the methodology for the quantification of the local bonding configuration of carbon on the basis of NEXAFS data is still lacking.

In the present study [1], the common methodology for quantitatively evaluating the carbon hybridization state using carbon 1s NEXAFS measurements, which is based on the analysis of the sample of interest and of a highly ordered pyrolytic graphite (HOPG) reference sample, is reviewed and critically assessed, noting that inconsistencies are found in the literature in applying this method. A theoretical rationale for the specific experimental conditions to be used for the acquisition of HOPG reference spectra is presented together with the potential sources of uncertainty and errors in the correctly computed fraction of  $sp^2$ -bonded carbon. This provides a specific method for analyzing the distribution of carbon hybridization state using NEXAFS spectroscopy. As an illustrative example, a hydrogenated amorphous carbon (a-C:H) film was analyzed using this method. The comparison of the NEXAFS results with the outcomes of X-ray photoelectron spectroscopy (XPS) and Raman



measurements revealed good agreement between the analytical results, which validates the method and further indicates the absence of a structurally different near-surface region in this thin-film material

The present work can assist surface scientists in the analysis of NEXAFS spectra for the accurate characterization of the structure of carbon-based materials.



**Figure 1.** During an electron yield near edge X-ray absorption fine structure (NEXAFS) spectroscopic measurement the sample is irradiated with monochromatic X-rays. The energy of the X-rays is varied around the ionization edge of the element of interest. By measuring the number of emitted Auger electrons as a function of the energy of the incident X-rays, a NEXAFS spectrum is collected. Absorption features are observed when the energy of the incoming photons matches the energy difference between the initial state and an unoccupied (molecular) state. In the case of carbon-based materials, such as hydrogenated amorphous carbon (a-C:H) films, carbon 1s NEXAFS spectra can be effectively used to gain insights into the carbon hybridization state, the local ordering, and the degree of hydrogenation. The present study aims to review and critically assess the common methodology for quantitatively evaluating the carbon hybridization state using carbon 1s NEXAFS measurements.

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## An analytical study for the conservation of the Matera Cathedral

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To afford the restoration and conservation of Santa Maria della Bruna and Sant'Eustachio Cathedral in Matera, an investigation of the state of conservation material used for past restoration interventions, was performed. In fact, the façade, was affected by thick black encrustations, particularly in the lower part, as shown in Figure 1. The multi-analytical approach was the following:

- preliminary investigation with on-site portable diagnostic systems, which permitted to select representative samples to be collected by scalpel;
- laboratory analysis for the determination of the inorganic material by means of X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) and for the characterisation of the organic material by means of Gas Chromatography/ Mass Spectrometry (GC/MS);
- evaluation of the efficacy and durability, of some protective and/or consolidant commercial products, for a successful protective action of the Cathedral surface.

The analysis evidenced the presence of a proteinaceous material, which underwent degradation phenomena, contributing to the formation of thick black patina. The X-ray diffraction and the Fourier Transform Infrared Spectroscopy, allowed the identification of its inorganic composition.

After the cleaning procedure of the Cathedral, some products for stone protection were chosen. The selected products (Pulvistop and Idrobloc by Geal S.r.l., Hydrophase Acqua by Phase Italia) were aqueous emulsions of silanes/siloxanes having low and medium molecular weight, with water repellent and consolidant (Pulvistop only) properties for stone materials. In order to study the polymerisation degree, the products were applied both on blocks of organogenic limestone (pietra di Matera) specifically extracted from the monument, and laboratory model. The products applied on glass microscope coverslips have been submitted to artificial aging in Solar Box (CO.FO.ME.GRA 3000e, equipped with Xenon lamp,  $\lambda > 295$  nm) for 1000 h at  $500 \text{ W/m}^2$ , in order to test their resistance to UV irradiation. The protective materials applied on the portions of the stone block (22 wide x 23 height X 3,5 cm thickness) have been positioned in outdoor for the natural aging (in July/August 2015), with an angle of  $30^\circ$  respect to horizontal plane, with the treated face facing S-SE. A Pyroprobe EGA/PY-3030D (Frontier Lab) coupled with a Gas Chromatograph/ Mass Spectrometer (Agilent technology) has been used for the characterisation of the fresh and the both artificially and

naturally aged products. The interpretation of the pyrolysis pattern of the natural aged materials, revealed the absence of significant oxidation and crosslinking products, moreover it was also assessed that the Idroblock and Hydrophase resins are present in very small amounts on the stone surface. Finally the study of the artificially aged resins, helped us in suggesting the siloxane resin Hydrophase with a low molecular weight to be used as protective for the conservation of this masterpiece of Italian art.

Acknowledgments. The authors thank D'Alessandro Restauri s.r.l. and Giancarlo Ranalli (Università degli Studi del Molise) for the involvement in this important conservation work.



**Figure 1.** The façade of the Santa Maria della Bruna and Sant'Eustachio Cathedral in Matera.

**Inductively coupled plasma mass spectrometry as a powerful tool  
for the determination of arsenic and selenium species  
for environment, food and health**

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Trace elements play important roles in many aspects of environmental and human health ranging from essentiality to toxicity. In particular, arsenic is of great interest because it derives from both natural and anthropogenic sources and its toxicity and bioavailability are strongly dependent on its chemical form. Another important element, selenium, is essential for human health, but the boundary between its essential and toxic levels is extremely narrow, and the resulting biological effect depends on both the amount and the chemical form it is ingested and/or transformed. Hence, it can be easily understood that speciation studies are necessary for toxicological and environmental considerations, while the determination of total arsenic and selenium is not sufficient for this purpose.

Inductively coupled plasma mass spectrometry (ICP-MS) is the technique of choice for elemental analysis, offering many advantages in terms of robustness, sensitivity, wide linear range and minimum sample purification requirements. ICP-MS is usually coupled to high performance liquid chromatography (HPLC) for the separation of the different species, representing a well established approach for speciation analysis, but it is limited by the low tolerance of the detection system to mobile phases with high salt content or organic solvents.

In this work we present our studies on new analytical methods for the determination of arsenic and selenium species in different matrices of environmental, food and health interest. In particular, the drawbacks of the HPLC-ICP-MS coupling have been overcome with two different approaches. The first one is the application of high temperature liquid chromatography<sup>2</sup> (HTLC), where the mobile phase is heated up to get faster separations and better resolution; moreover, organic solvents or saline solutions can be replaced by pure water as the mobile phase, thus making HTLC cheaper, simpler, more environmental friendly and suitable to ICP-MS than conventional HPLC. The second one is the reduction of mobile-phase flow rates (narrow bore columns), with a thorough study of the effects of low liquid flow rates on the analytical signal of the different species.

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# Oral presentations

## **New developments in Quartz enhanced photoacoustic gas sensing in the Infrared and THz spectral ranges**

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Quartz-enhanced photoacoustic spectroscopy (QEPAS) is a very powerful technique that allows selective and sensitive measurements of trace gases in an ultra-small acoustic detection module (ADM) with a total sample volume of only a few mm<sup>3</sup> [1]. The principle of this technique is based on the photoacoustic (PA) effect, where the absorption of modulated laser radiation by gas molecules causes a periodic heating of the chemical species. The heating results in thermal expansion, and leads to a pressure change in the targeted media. The generated pressure wave is detected by a quartz tuning fork (QTF) acting as sharply resonant piezoelectric transducer.

I will report an overview of the latest developments in QEPAS trace-gas sensor technology such as the design and realization of custom QTFs with different geometries providing an enhancement of photoacoustic generation efficiency [2], QEPAS sensors operating in QTF first overtone flexural mode [3] and QEPAS sensors employing a single-tube acoustic micro-resonator providing an improvement of the detection sensitivity by two orders of magnitude compared to a bare QTF [4].

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## Detection of foodborne pathogens by optical biosensing

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Due to an increasing occurrence of foodborne diseases, the rapid detection of foodborne pathogens is highly desired to minimize outbreaks and ensure food safety and consumers' health [1,2]. Conventional methods for the detection and identification of pathogens rely on time- and effort-consuming steps, exploiting biochemical or serological identification [3]. SPR optical biosensors have been shown to represent good alternatives to traditional methods for pathogen detection [4]. SPR is a label-free technique for probing molecular and macromolecular interactions [5]. SPR imaging extends capabilities of traditional SPR, by using a CCD camera for signal detection and simultaneous analysis of different interactions [6]. Recently, the use of gold nanoparticles (AuNPs) in combination with peptide nucleic acid (PNA) probes allowed the ultrasensitive detection of genomic DNA (gDNA) [7,8].

In this communication, we describe the use of nanoparticle-enhanced SPRI biosensing for the detection of foodborne pathogen gDNA. The sensing strategy relies on the use of highly specific PNA sequences and AuNPs properly conjugated to an oligonucleotide sequence complementary to the tract of the pathogen gDNA not involved in the hybridization with the surface-immobilized PNA probe. Preliminary studies performed with an oligonucleotide sequence related to pathogen DNA (ssDNA) demonstrate that it is possible to apply the same sandwich hybridization strategy to the detection of pathogen gDNA.

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## Spectroscopic and morphological characterization of antibacterial properties of Ag-fluoropolymer thin films by AFM and IR-ATR spectroscopy

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In this work, Ag-Teflon-like (Ag-CF<sub>x</sub>) composite materials with different metal loadings ( $\phi$ ) were obtained on different substrates by ion beam co-sputtering of polytetrafluoroethylene (PTFE) and Ag targets. Ag was chosen because of its antimicrobial activity and easy availability<sup>1</sup>. On the other hand, Teflon-like materials present hydrophobic surfaces with additional anti-stain features. As a result, Ag-CF<sub>x</sub> nanostructured coatings possess characteristics of both components, being highly appealing for the development of high-performance nanoantimicrobials. In recent years, applications of nanocomposites such as (polymeric) matrix that immobilizes NPs have gained significant importance in everyday products. In fact, it can prevent and/or limit human exposure to entire NPs. Despite the many benefits of antimicrobial NPs, many studies indicate that they might cause adverse toxic effects in human organs, as well as DNA damage<sup>2</sup>.

Here we present a full characterization of such materials. Morphological characterization was obtained by transmission electron (TEM) and atomic force (AFM) microscopy, which showed that Ag cluster size did not increase with  $\phi$ , and no nanoparticle aggregation or percolation paths were observed at high loadings. XPS characterization revealed that a quite branched polymer dispersing matrix was produced; but, no evidence of metal fluorides were found on the composite surface, in contrast to other metal-fluoropolymer thin films<sup>3</sup>. Electro-thermal atomic absorption spectroscopic (ETAAS) studies for quantification of the Ag(I) ions released in physiologic solution showed a 1<sup>st</sup> order release kinetic, with a slight correlation with plateau silver concentrations and inorganic loading. Bioactivity of the presented nanocoatings was also assessed against *P. fluorescens* microorganism. Biofilm growth was monitored by attenuated total reflectance-infrared (ATR-IR) measurements with a flow-through cell and the characteristic IR bands associated to biofilm development were acquired as a function of time. Subsequently, biofilm inhibition was assessed using an Ag-CF<sub>x</sub>-modified waveguide. The thin film was deposited onto the ZnSe crystal after the identification of its IR-inactive areas. This procedure is of outmost importance to avoid affecting the IR signal quality within the waveguide surface<sup>4</sup>. It could be shown that the antimicrobial nanocoating effectively suppressed the *P. fluorescens* biofilm formation within about 2 hours. Those results were fully corroborated by AFM imaging of bacteria incubated onto Ag-CF<sub>x</sub>-films. Bacterial surface roughness strongly increased with the incubation time, indicating a severe bacterial stress induced by the composite film. For long contact times,

silver nanoclusters were found homogeneously covering the bacterial surface; their composition was confirmed by scanning electron microscopy-energy dispersive X-ray (SEM-EDX) measurements of the dried samples after AFM measurements.

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## **Assessment of corrosion inhibition by X-Ray Photoelectron Spectroscopy and Electrochemical Impedance Spectroscopy**

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The environmental protection and the preservation of the health of professionals are key issues to be addressed for a sustainable scientific approach to the conservation of Cultural Heritage. Nowadays, new green and low toxic corrosion inhibitors for the conservation of metallic artifacts should be available for replacing the presently used hazardous materials. In recent past years a consolidated collaboration between CNR (Italy) and CNRST (Morocco) was carried out for investigating both chemically synthesized and naturally-derived products as corrosion inhibitors [1,2].

The aim of this work is to show how spectroscopic analytical techniques, such as X-Ray Photoelectron Spectroscopy (XPS) and Electrochemical Impedance Spectroscopy (EIS), can be successfully applied for assessing the corrosion inhibiting properties of new green formulations for the conservation of metallic artworks.

X-Ray Photoemission Spectroscopy (XPS), widely used in the field of industrial research, can be usefully applied in the field of Cultural Heritage in order to define the nature and the state of conservation of artifacts, and to propose and validate innovative materials and methods for conservation and restoration. The application of such a surface-sensitive analytical technique can provide extremely important information, especially on the presence of patinas and alteration/degradation products, on the efficacy of protective coatings and corrosion inhibiting treatments.

The Electrochemical Impedance Spectroscopy (EIS) is one of the most powerful technique for characterizing the electrical properties of both liquids and solid materials and for understanding electrochemical and electronic processes occurring at the electrode/electrolyte interface [3]. It is widely used in the study of metals and alloys corrosion and protection by organic coatings and paints as it provides the main kinetic parameters connected to corrosion and to corrosion inhibition processes. In Conservation Science electrochemical techniques are well-suited for two general purposes: i) as analytical methods in order to determine the original composition of the materials, their alteration or corrosion products, to assess prior restorations treatments and to evaluate the performance of new products as corrosion inhibitors; ii) as restorative/conservative methods in order to restore the original state and/or incorporate protective materials for ensuring the future conservation of the artwork.

In this work a new green formulation based on the oil extracted from the seeds of *Nigella Sativa L.*, a widespread plant in the Mediterranean basin, was tested as corrosion inhibitor for bronze and iron artifacts in chlorides and acidic media, respectively. Films of this formulation on iron and bronze substrates were produced by immersion at room temperature and then submitted to corrosion by rain water solution and by an aggressive 3% NaCl solution, respectively [4-6].

The electrochemical behavior was investigated in a chlorides or rain water media, both in presence and absence of the natural inhibitor formulation. Experiments were performed as a function of the concentration and of the immersion time. The best performance of the green formulation was ascertained in the case of iron corrosion by acidic medium. Results showed that the formulation acts as a good mixed type (cathodic/anodic) inhibitor. The dissolution rate decreased with the increase of both the concentration and the immersion time. An inhibition efficiency of 99% was reached for a concentration of 2500 ppm.

The chemical characterization of the films surface was performed by XPS both before and after submission to the corrosion attack. Surface results confirmed a good protective action of the formulation, both on the iron and bronze substrates. Acute toxicity tests proved that the formulation is a non-toxic and environmentally safe product (LD50 > 6000 mg/kg), usefully suitable for a sustainable conservation of iron artifacts.

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## **Purple photosynthetic bacteria and sea urchin coelomocytes examination by X-ray photoelectron spectroscopy as a non-conventional analytical technique for bio-organic materials**

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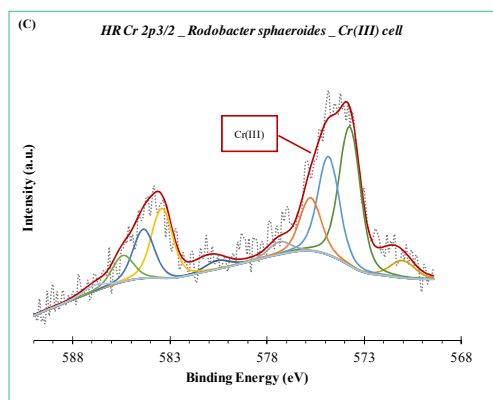
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In this study, we report some preliminary results on the X-ray photoelectron spectroscopy (XPS) characterization of photosynthetic bacteria and sea urchins coelomocytes. XPS spectroscopy is a surface technique that allows to analyze, in terms of chemical speciation, all elements, with the exception of H and He, present in different typologies of solid samples (inorganic and organic), as long as their atomic percent concentrations (At.%) are not below 0.01-0.1%, depending on the specific element. This technique potentially can also allow to obtain chemical imaging of surfaces with lateral resolution of 3 $\mu$ m. However, at the state of the art, the employment of this analytical technique as a non-conventional tool for the investigation of bio-organic materials (i.e. microorganisms and their related systems such as biofilms, extracellular polymeric substances (EPS) and bio-adhesions), has been reported only in a limited number of papers[1].

The XPS characterization of purple photosynthetic bacteria (*Rhodobacter sphaeroides*), able to interact with detrimental heavy metal ions, such as nickel and chromium has been performed, leading to the successful detection of both metal immobilization and surface modifications induced by the environmental stress. Measurements revealed that treatment with Ni<sup>2+</sup> results in full displacement of K<sup>+</sup> ions from *R. sphaeroides* bacterial surfaces, indicating high affinity between nickel ions and surface functional groups. Moreover the detection of chromium(III) onto *R. sphaeroides* cells (Figure 1) incubated with chromate ions allowed to confirm the potential of this phototrophic bacterium as bio-catalyst for the reduction of chromate to the less toxic trivalent form

Furthermore, the sea urchin *Arbacia lixula* coelomocyte population is characterized by the presence of red cells, which number may increase in response to different stress. As red spherula cells accumulate around injuries and sites of infection, this analysis may help to understand what is the role of cell surface interacting with bacteria in addition to the action of echinochrome A present inside the cells. In particular, here we compare the red cells coelomocytes surface with the white ones, highlighting a quite different surface chemical composition.



**Figure 1.** Cr 2p XPS peaks from *R. sphaeroides* cells after Cr(VI) exposure and attributed to Cr(III)[2].

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## **Electrosynthesis, spectroscopic characterization and biological evaluation of Gallium- or Silver- modified chitosan coatings on titanium implants**

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Microbial colonization and delayed osteointegration are the most frequent causes of orthopaedic implant failure<sup>1,2</sup>. The local delivery of antibacterial agents represents an effective approach to prevent infections, avoiding the side effects of systemic antibiotic therapy<sup>3</sup>. On the other hand, the presence of osteoblasts inductors onto the implant could improve osteointegration, strengthening the mechanical stability of the prosthesis<sup>4</sup>.

In this work, a novel polymeric bilayer is proposed as titanium coating able to optimize the implant performances in the biological environment. The coating consists in a poly(acrylic acid) layer electrosynthesized directly on titanium, furtherly covered by a chitosan layer obtained by chronoamperometry. The superficial chitosan layer is loaded with silver or gallium ions: while the former have a powerful antibacterial activity, the latter are promising activators of the osteointegration process. Combined with chitosan and poly(acrylic acid) biocompatibility, these ions may confer to titanium implants additional features, helpful to hinder bacterial colonization or to enhance prosthesis fixation through bone matrix deposition.

An accurate analytical characterization of the bilayer has been performed by XPS, ATR-FTIR, and AFM techniques, while antibacterial properties and cytotoxicity studies have been investigated *in vitro*. XPS and ATR-FTIR spectroscopic studies show bilayer spectra similar to those of chitosan, with a detectable poly(acrylic acid) contribution. Furthermore, AFM investigations reveal the formation of a homogeneous coating on titanium. SEM morphological analysis and MTT viability test show well adhered MG63 osteoblast-like cells, with a good cell viability on the gallium-loaded bilayer. On the other hand, the silver-loaded bilayer provides a powerful antibacterial activity although the cytocompatibility could be improved.

The multifunctional coatings described in this work represent a promising strategy to address infections and osteointegration delay, improving the clinical performances of titanium orthopaedic implants.

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## Silicon Nanowires: Synthesis, structural properties and photonic applications

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Silicon nanowires (NWs) are attracting the interest of the scientific community as building blocks for a wide range of future nanoscaled devices. We demonstrate the synthesis of NWs by a cheap, fast and maskless approach compatible with Si technology, using metal-assisted chemical etching of Si substrates catalyzed by thin metallic layer. Using percolative Au layers that exhibit a fractal arrangement as the catalyst of a metal-assisted wet etching process, we achieved a 2D random fractal array of vertically aligned Si NW, realized without any lithographic process. By designing different fractal textures through the optimization of NW size and spatial arrangement, we were able to control and tune the optical properties of the system. Strong in-plane multiple scattering and efficient light trapping related to the fractal structure were observed [1]

NWs obtained by this method have tunable nanometer-size diameter, suitable to observe quantum confinement effects, indeed a bright room temperature PL is reported. The realization of Si NWs-based light emitting devices has been demonstrated, showing an efficient room temperature electroluminescence emission at low voltage. The decoration of NWs with silver nanoparticles by pulsed laser ablation technique is presented. We demonstrated that the union between the huge surface-to-volume ratio of the Si NWs material and the plasmonic properties of silver nanoparticles unveils advantageous for the use of this unconventional 3D material for ultrasensitive Surface Enhanced Raman Scattering applications with respect to a standard substrate.

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## **Nanoparticles Enhanced Laser Induced Breakdown Spectroscopy: concepts and applications and prospectives.**

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The development of knowledge on nanotechnology is having a great impact in analytical chemistry like in mass spectrometric techniques, SERS, high resolution microscopy and gas sensors. Nanometric scale of particle dimension causes peculiar physical features for what concerns their electrical, optical and thermal properties that have been intensively investigated in the last decade.

Starting from these considerations we have recently proposed, for the first time, Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy (NELIBS) [1,-3] in order to enhance the efficiency of the laser-matter interaction consequently increasing the emission LIBS signal. NELIBS is based on the deposition of a colloidal solution of noble metal NP on the sample surface and virtually does not require any change in the LIBS set-up. As examples in the case of conductor sample, NELIBS allows a signal enhancement up to tow orders of magnitude as a consequence of electron field emission during the laser-matter interaction, while in the case of transparent medium, it is possible to obtain enhanced spectra with respect to conventional LIBS without damaging or cracking the sample itself as a consequence of changes in the optical properties. Finally NELIBS has been applied to solution analysis and molecular detection enhancing the sensitivity of the LIBS to more than one order of magnitude enabling an absolute LOD of less than a picograms.

In this work the fundamental aspects of NELIBS is be discussed in correlation with quantitative analysis of different kind of samples (metals and alloys, glasses, solution, biological solution and molecules). Further prospective of nanoparticles applications to LIBS will be discussed as well.

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## X-ray Photoelectron Spectroscopy as a new tool to study cell uptake of inorganic nanoparticles

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In recent years, 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 physical and chemical properties, including optical, electrical, and magnetic properties.[1]

The reason why these nanoparticles (NPs) are attractive for medical purpose is based on their ability to absorb and carry other compounds. 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. Source material may be of biological origin like phospholipids, lipids, lactic acid, dextran, chitosan, or have more “chemical” characteristics like various polymers, carbon, silica and metals.[2]

However, although nanoparticle-based DDSs offer many advantages, 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 many studies of NPs uptake/release *in vitro* on cells culture are performed using “conventional” techniques such as confocal microscopy, transmission electron microscopy (TEM) or Inductively Coupled Plasma (ICP). However these methods could require further treatments in order to be utilized such as functionalization step to add fluorescent label that can modify NPs composition [1], complex treatment in order to be analyze [3] or poor information about localization of NPs as in the case of ICP. Moreover 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) and angle resolved XPS (AR-XPS) allowed us to measure the change in the concentration of various elements as a function of depth into the sample. Depth profile analysis is a powerful tool for probing the composition and elemental and chemical structure of cells loaded with NPs.

This technique is useful to understand the biological interactions of nanoparticles in contact with the cells and the oxidation state of elements. In this way it is possible to have

information about toxicity and internalization of nanoparticles depending on their synthesis and functionalization procedures [4].

A dispersion of different NPs in the cell culture medium has been studied. Comparison with unloaded cell will be discussed as well.

Currently, analysis about the study of interaction NPs - cell membranes and mechanism of cellular uptake/release are in progress.

To the best of our knowledge this is the first attempt to study inorganic nanoparticles cell uptake by means of XPS.

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## Single particle ICPMS for nanoparticle analysis in various matrixes

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Single particle ICPMS is a revolutionary way to analyze directly nanoparticle, the fast data acquisition of the modern ICPMS system allows fast nanoparticle sizing through the direct sample analysis.

The lecture will give some analytical evidences of single particle analysis in sizing and distribution of nanoparticles of Silver, Iron and Silicon in environmental and biological matrices.

## Human exposure to thallium through tap water: a study from Valdicastello Carducci and Pietrasanta (northern Tuscany, Italy)

Beatrice Campanella<sup>1,2</sup>, Massimo Onor<sup>1</sup>, Alessandro D'Ulivo<sup>1</sup>, Roberto Giannecchini<sup>3</sup>,  
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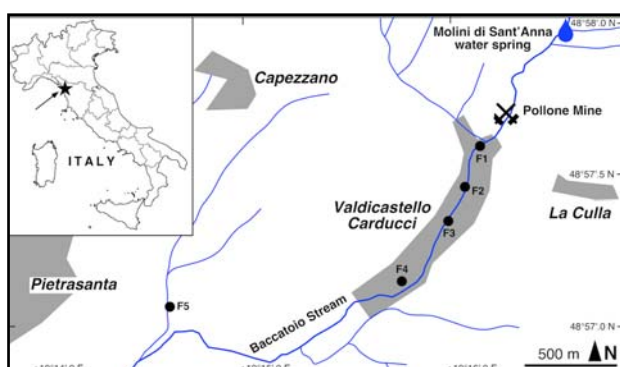
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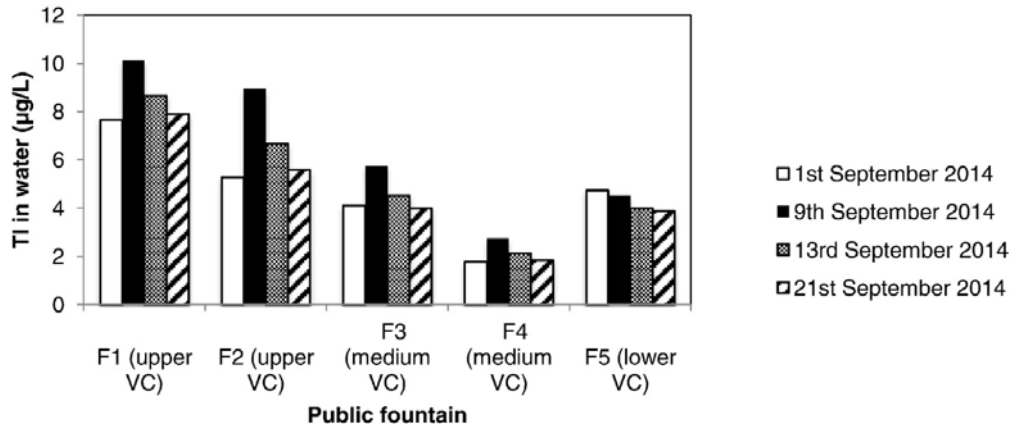
A geological study evidenced the presence of thallium (Tl) at concentrations of concern in groundwaters near Valdicastello Carducci (Tuscany, Italy). The source of contamination has been identified in the Tl-bearing pyrite ores occurring in the abandoned mining sites of the area. The strongly acidic internal waters flowing in the mining tunnels can reach exceptional Tl concentrations, up to 9000 µg/L. In September 2014 Tl contamination was also found in the tap water distributed in the same area (from 2 to 10 µg/L). On October 3<sup>rd</sup> 2014 the local authorities imposed a Do Not Drink order to the population.

Here we report the results of the exposure study carried out from October 2014 to October 2015, and aimed at quantifying Tl levels in 150 urine and 318 hair samples from the population of Valdicastello Carducci and Pietrasanta. Thallium was quantified by inductively coupled plasma – mass spectrometry (ICP-MS). Urine and hair were chosen as model matrices indicative of different time periods of exposure (short-term and long-term, respectively).

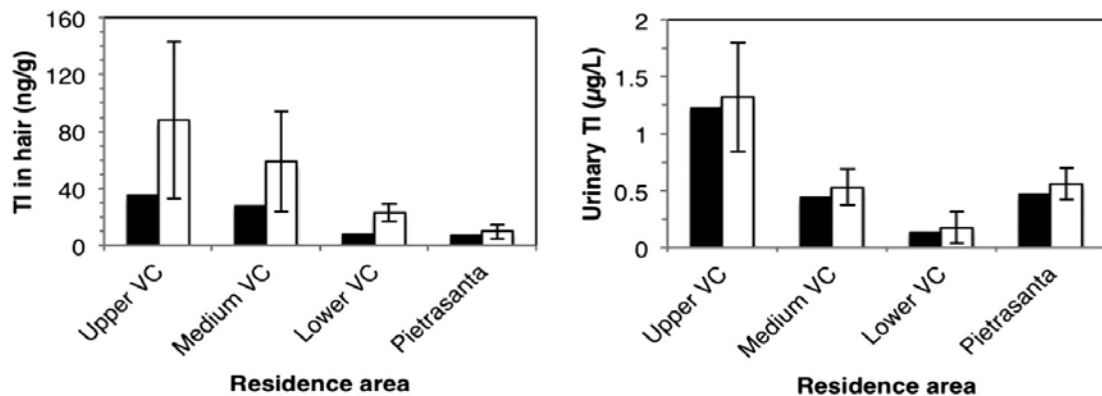
Thallium values found in biological samples were correlated with Tl concentrations found in tap water in the living area of each citizen, and with his/her habits. Thallium concentration range found in hair and urine was 1 – 498 ng/g (values in unexposed subjects 0.1 –6 ng/g) and 0.046 – 5.44 µg/L (reference value for the European population 0.006 µg/L), respectively. Results show that Tl levels in biological samples were significantly associated with residency in zones containing elevated water Tl levels. The kinetics of decay of Tl concentration in urine samples was also investigated. At the best of our knowledge, this is the first study on human contamination by Tl through water involving a such high number of samples [1].



**Figura 1.** Sketch map showing the localities cited in this work. F1 to F5 are the public fountains whose water was analyzed for this study (fountain F6 is located close to the Pietrasanta cemetery, outside the map).



**Figure 2.** Levels of TI measured in tap water collected from 5 public fountains in Valdicastello (F1-F2: upper Valdicastello; F3-F4: medium Valdicastello; F5: lower Valdicastello) sampled during September 2014.



**Figure 3.** Arithmetic mean (white bars) with standard deviation and geometric mean (black bars) of TI levels found in hair (a) and urine (b) classified according to the residence of the subjects.

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## **Spectroscopic analyses of foods with a low environmental impact**

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In the last few years a sector of Spectroscopic 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. In this 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. An application example is represented by the analytical systems which specialize and optimize the photometric technology in terms of cost, of the amount of reagent used, and of time. Such systems are based on the use of "micromethods", involving the use of small quantities of the sample used for the analysis and a consequent significant decrease in the consumption of chemical and biochemical reagents. If they are compared with traditional reference methods, they determine a considerable reduction of waste to be disposed. The advantages of micromethods, combined with a multivariate optimization of analytical procedures allow to make quality controls directly on the food production line and no longer require the transfer of samples to remote laboratories, thus saving time and increasing the efficiency of control, especially in the measurement of dynamic parameters in rapid evolution as in oxidative processes. In particular the multivariate optimization has the aim to determine the type and quantity of pre-dosed and pre-put-into-phials reagents so as to obtain an optimal process. The simplification and the low energy impact of the analytical protocols allow to develop new techniques of appreciation of oxidative stability, as shown by the study of olive oil samples from the Laboratory of Analytical Chemistry of the University of Athens [1], as an alternative to the traditional methods, which, applied on production chain, determine as a result the improvement of the quality level of the food product. Also, rapid measurement methods of biophenols content in extra virgin olive oil were developed; these methods have been found to have a very good correlation with the international reference methods [2].



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## **Combined biological assays and X-ray spectroscopy techniques to assess the bioavailability of arsenic in two industrial contaminated soils**

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Arsenic (As) is a metalloid, naturally associated with gold, sulphur, iron and heavy metals and is often found in soils and wastes around former mines and industrial sites because of the processing of As-bearing minerals. Assessment of the bioavailability of As in these soils is very important in order to protect human and ecosystems health. Earthworms are often used to assess the bioavailability of As in soils (Langdon *et al.*, 2003). In this work, *Eisenia andrei* was exposed to As-polluted soils from Valle Anzasca and Scarlino (Italy) in order to evaluate the bioavailability of As. Different X-ray based techniques were used to evaluate the concentration and the distribution of As both in soils and earthworms.

For this study, three soil samples per polluted site were collected, sieved (2 mm) and dried. The mineralogical characterization of soils was carried out by X-ray powder diffraction (XRPD). The total As was estimated *on site* via portable X-ray fluorescence (XRF), while sequential extractions (Wenzel *et al.*, 2001) coupled with total reflection XRF (TXRF) were used to study the mobility of As. Soil elemental maps were acquired using micro XRF ( $\mu$ XRF) in order to evaluate the As distribution and its correlation with other elements. All the above analyses were conducted also on two control soils.

For the assessment of the bioavailability, ten sexually mature earthworms were exposed to each contaminated soil and controls. The mortality was assessed after 14 days of exposure (acute toxicity). Oxidative stress was estimated by measuring  $H_2O_2$ , catalase, phenoloxidase, glutathione S-transferase and malondialdehyde. The effect of As on the reproduction (chronic toxicity), was assessed after 28 days of exposure. Earthworms were embedded in epoxy resin and thin sections (100  $\mu$ m thickness) were analyzed via  $\mu$ XRF in order to localize As accumulation. Since detoxification mechanisms seem to act mainly inside the coelom (e.g. for Cd, Panzarino *et al.*, 2016), coelomic fluids (few  $\mu$ l) were electrically extruded from worms and analysed by TXRF in order to quantify the As concentration.

The mineralogy of soils from Valle Anzasca (V1, V2, V3) is uniform and characterized by the presence of illite, quartz, albite and orthoclase. Two Scarlino soils are characterized by the presence of illite, kaolinite and quartz (S1 and S2) while gypsum and magnetite have been also detected in S3. No As-bearing mineral was detected by XRD in all the six soils. However, sequential extractions results (Table 1) showed that As is mainly associated with amorphous Fe-hydrous-oxides, and this fraction increases with the increase in As concentration in Valle Anzasca soils. Differently, in Scarlino soils, As is mainly associated with well-crystallized Fe hydrous-oxides, except in S1 where the total As concentration is low (41 mg/kg). This is confirmed by  $\mu$ XRF maps which show an overlap between Fe and As, probably precipitates, around quartz or feldspar grains.

Biological tests showed that no organism died after a period of 14 days exposition to As-contaminated soils. However, reproduction tests evidenced a reduction of the number of

new born earthworms with the increase of As concentration in soil. An oxidative stress was recorded in all the earthworms exposed to contaminated soils, without evidence of a concentration effect, while no stress was detected in organisms exposed to control soils.

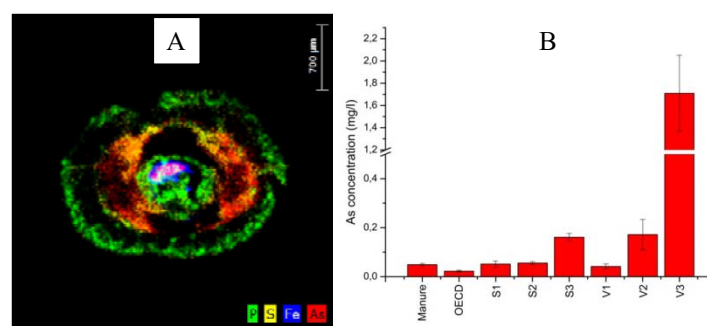
Elemental maps acquired on earthworm sections by  $\mu$ XRF (Figure 1A) showed that As is found in the coelomic cavity together with S. No As signal is recorded in other parts of the earthworms grown in contaminated soils. The co-presence of Fe and As in the intestine is due to the presence of soil residues.

The concentrations of As in coelomic fluids (Figure 1B) increases with the amount of arsenic in soils, although the type of association between As and Fe-hydrous oxides seems to be crucial. When a consistent part of the As is associated with well crystallized Fe-hydrous oxides, the concentration of As in the coelomic fluids is comparable to that found in the coelomic fluids of earthworms exposed to control soils. On the contrary, when the As is associated with amorphous iron hydrous oxides, the concentration of As in coelom increases considerably compared to control samples.

The methods described could be used in ecotoxicology studies where earthworms serve as bioindicators of As pollution in soils with different degree of contamination. Further biological analysis should be performed in order to assess the eco-toxicity of As.

**Table 1.** Relative percentage of As in each extraction step and total As concentration estimated with portable XRF .

Extraction step	S1	S2	S3	V1	V2	V3
1. Non-spezif. sorbed	0	0	1	2	1	0
2. Specif. sorbed	15	4	12	11	25	12
3. Amorphous h-ox of Fe	46	3	41	50	67	85
4. Well-cryst. h-ox of Fe	0	90	42	28	2	1
5. Residue	38	3	4	9	6	1
Total As (mg/kg)	41	224	736	134	3174	9135



**Figure 1.** Distribution of P, S, Fe and As in a cross section of an earthworm grown in V3 for 28 (A) and Concentration of As in coelomic fluids determined by TXRF(B).

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## Determination of total and free cyanide in soil by isotope dilution gc/ms following pentafluorobenzyl derivatization

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Hydrogen cyanide and its salts are well known powerful toxic agents for living organisms. Its high toxicity together with its relevant industrial use fuelled the interest for the development of straightforward analytical methods for its determination.<sup>1</sup>

Here we propose a method for the determination of cyanide with several interesting unprecedented/novel features. Cyanide was quantified in soil samples after a single-step derivatization with pentafluorobenzyl bromide (PFB-Br) followed by identification with gas chromatography – negative chemical ionization mass spectrometry.

Fundamental and clarifying aspects of the PFB-Br derivatization of cyanide were investigated. The effects of some parameters on the derivatization step were established in order to achieve the selective formation of the trialkylated nitrile,  $(C_6F_5CH_2)_2C(C_6F_5)CN$ .

An easy and time-saving configuration based on a micro-distillation strategy was developed for cyanide extraction from soil, which guarantees operator safety along with matrix removal and a quantitative recovery. 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 cyanide in certified reference materials of contaminated soil using commercial  $K^{13}C^{15}N$  as internal standard.

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## **Calibration-Free quantitative analysis of Antoninianus coins by Laser-Induced Breakdown Spectroscopy (LIBS) in depth-profile mode.**

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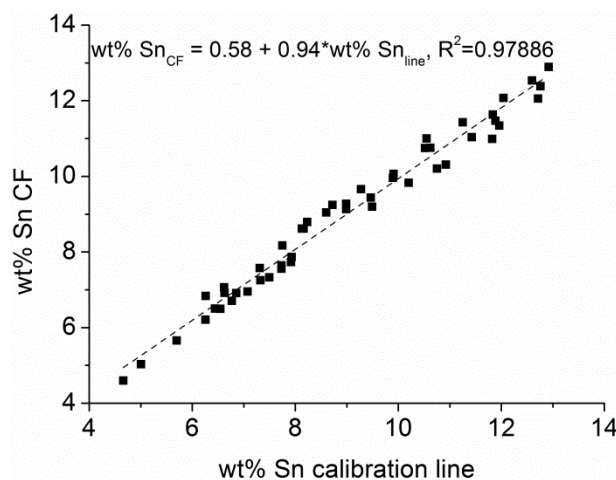
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Laser-Induced Breakdown Spectroscopy (LIBS) features several characteristics that can make it a technique of choice in the field of cultural heritage diagnostics and archaeometry, such as: micro-destructivity (ablated mass per pulse in the order of hundreds of nanograms); possibility of performing in situ and stand-off analyses, even in extreme environments; simultaneous detection of major and minor elements, included light ones; possibility of calibration-free measurements; possibility of depth-profile analyses [1-2]. In this work, we have exploited LIBS for the elemental analysis in depth-profile mode of a series of Antoninianus coins from Egnatia (Apulia, Southern Italy). In particular, we were interested in studying the effect of Aurelian' monetary reform (274 a.D.) on the Ag content and in obtaining information about the progressive debasement that these coins experienced after their introduction under Caracalla's (Antoninus Pius) reign. A novel LIBS method was used to carry out these analyses, i.e. the calibration-free inverse method (CF-IM) that was recently developed [3,4] for the determination of plasma temperature and elemental composition, and suitably adapted to depth-profile analyses. The CF-IM belongs to the family of CF approaches, first proposed by Ciucci et al. [5], and it may be considered as halfway between the actual CF methods and the classical calibration line approaches, because it requires the use of a single calibration standard. We chose to operate with a CF approach because such methods are particularly useful in case of analysis of complex matrices, for which acquiring or preparing matrix-matched standards may be difficult or impossible. In this work, the calibration standard, that in the case of the IM does not have to be necessarily matrix-matched, was used as a sort of reference sample to determine the plasma temperature and model the acquisition conditions of the spectra. Thus, a depth profile of the standard sample was performed in order to obtain a plasma temperature profile, which in turn we employed, together with the analogous electron density profile, for the calibration-free analysis of the coins. The methodology was validated by comparing the CF results with those of classical LIBS, i.e. by drawing calibration lines with a series of certified standards for elements that were present in the standard themselves (see for example figure 1, where the correlation line of Sn is reported). The obtained results showed that all the analyzed samples were made of a Cu/Ag/Sn/Pb quaternary alloy, copper being the main alloying element. Interestingly, virtually no difference was detected for the Ag content between pre- and post-reform

samples, while the Sn content resulted clearly different, around 10% in the pre-reform coins and around 4 % in the post-reform ones.



**Figure 1.** Correlation plot between CF and calibration line results for Sn weight percentage (wt%).

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## Characterization of zinc carboxylates in modern paintings at the macro and micro-scale by FTIR spectroscopy

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Oil paintings often suffer deterioration phenomena due to the formation of metal soaps, originated from the reaction between pigments and the oil binder. Pigment losses, changes in surface texture, increase of brittleness as well as delamination of the paint layer are frequent dangerous effects of the soap formation.

Zinc white (ZnO), one of the white pigments most commonly employed by nineteenth and twentieth century artists, demonstrated to react readily with the lipidic binder to give Zn-soaps. The presence of Zn-carboxylates has been proved in modern oil paintings by FTIR spectroscopy revealing the occurrence of different forms of zinc carboxylates characterized by sharp (typically at  $1540\text{ cm}^{-1}$ , generally assigned to Zn-stearate or -palmitate) or broad (at c.  $1580\text{-}1590\text{ cm}^{-1}$ ) bands in the antisymmetric carboxylate absorption region [1, 2].

In order to investigate the nature of the broad infrared feature, currently a topic of vivid scientific debate [3-5], different forms of Zn-carboxylates were reproduced in laboratory by preparing mixtures of ZnO and oil subjected to accelerated ageing (humidity and temperature). The analytical approach was based on the use of FTIR spectroscopy in different acquisition modes including transmission on KBr pellet and non invasive reflection directly from the model surface. Additionally, macro ATR-FTIR spectra were recorded on micro-samples, and micro-ATR-FTIR spectroscopic imaging was performed on unaged and artificially aged samples prepared as cross sections.

The comparison with other Zn-based compounds (ZnS and  $\text{ZnCO}_3$ ) evidenced that the peculiar broad band is strictly connected with the presence of zinc oxide and it appears at the early stage of the oil polymerization. In order to exclude any possible interaction with the additives or stabilizers, that maybe present in the commercial oil formulations, the same reactions have been followed using a pure triglyceride (trilinolein) and the corresponding alcohol ( $\gamma$ -linolenyl alcohol).

With the aim of investigating at a micro-scale level the formation and evolution of the different Zn-carboxylate forms in commercial paint formulations, some paint samples containing aluminum monostearate (one of the most common jellifying agent used in twentieth century oil paints) were investigated by micro-ATR-FTIR spectroscopy imaging. The study allowed for the spatial and spectral identification of the Zn-carboxylates on unaged and artificially aged samples. The comparison of the results obtained with the same micro-ATR-FTIR imaging and macro FTIR spectroscopy approach on a modern painting highlighted interesting analogies and differences improving the knowledge on this issue of crucial importance in the preservation of modern art.

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## **Spectroscopic studies of medieval wall paintings of Salento (Puglia, Italy): characterisation of pigment and techniques**

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The rupestrian civilization is a historical phenomenon of remarkable importance in many Mediterranean countries, and it is of considerable importance in various regions of Southern Italy. Extensive evidence of medieval rupestrian settlements are still preserved in Salento (Southern Italy), most of which have been dated to the 10th and 13th centuries; the churches, which can still be visited in the territory of the provinces of Lecce, Brindisi and Taranto (Puglia), were the results of the activity of Italo-Greek monks: they decorated their walls with images of the Virgin, Christ, bishops and other decorations referring to the style in vogue in the other provinces of the Byzantine Empire (Greece, Macedonia, Thrace and Anatolia). The wall paintings are of considerable artistic value, and the churches represent an important touristic place of Salento; however, many of their frescoes show significant conservation problems, such as dampness and capillary rise of water, biological attack, effluorescence, loss of the paint layer, especially the churches located below ground level (*crypts*).

Knowledge of raw materials and techniques used by the artists, and the state of conservation of the wall paintings is essential to plan correct restorations and preserve the extraordinary artistic patrimony. In the last years, several researches have been conducted on the Medieval wall paintings, especially in Greece, while in Italy Archaeometric studies are few, and the contexts have been better investigated from the historical and artistic point of view. Micro-Raman spectroscopy, compared to other analytical techniques, has numerous advantages, such as specificity, sensitivity, short analysis time, immunity to interference, high lateral resolution, not or micro-destructivity and the possibility to make measurements outside the laboratory with transportable instruments, even in severe conditions; Infrared spectroscopy allows to obtain also information on heterogeneous materials (organic and inorganic), it is micro or not-invasive method and does not require sample preparation, thanks to the use of the ATR crystal.

In this study different pictorial cycles of some important Medieval churches of Salento (*Santa Maria di Cerrate* and *Santi Stefani in Vaste*) were studied by spectroscopic techniques: portable Raman spectroscopy was used for identifications of pigments and degradation products *in situ*, while micro-Raman Spectroscopy and Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) were used in laboratory for the studies of few samples taken from selected scenes of the crypts, in order to obtain information also on the stratigraphic sequence and pictorial methodologies. The combined use of the two analytical techniques made it possible to reconstruct the palette and painting techniques; natural and artificial colours were used by the craftsmen and pigments were

applied both by fresco and egg-based tempera. Among the various pigments detected, the use of some of these was unexpected: it demonstrates a remarkable skill of the artists, evident from the use of mixtures of different pigments to produce the desired hue, from the overlapping of layers of different colours and from the use of fresco/secco techniques, and open new perspectives both from the historical and conservative points of view.

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## **An advanced FTIR method for the analyses of dyes micro-extracts**

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In the last decades, the analytical characterization of natural organic dyes in cultural heritage objects has gained a growing interest. Indeed dyes identification may support different studies on provenance, dating and production techniques of artworks and may provide information on suitable conservation treatments. Enhanced spectroscopic techniques have been developed in recent years for dyes identification in complex historical samples. In particular, SERS (Surface Enhanced Raman Spectroscopy) based methods allow to identify low amount of dyes due to the enormous enhancement of the Raman effect and to the quenching of the fluorescence which are both accomplished when the analyte is in direct contact with metal nanoparticles.

Recently we have proposed a FTIR enhanced method for the identification of dyes in micro-extracts [1]. Colloidal gold nanoparticles were mixed with the micro extract and spot into a gold coated glass slide for transfectance measurements.

In this paper we present a new enhanced sensitivity FTIR technique which allows analysis of dyed fibers micro extracts. We found that, when a film is some hundreds of nanometers thick and is applied onto a metal support, an enhancement of the signal is observed with respect to standard ATR as well as to transfectance. The angle of incidence should be just above the critical angle for the internal reflection of the element-sample interface. Simulations and experimental studies were performed on colorants belonging to four different classes (azo, triarylmethane, nitro and xanthenes). PCA elaboration allowed to underline the performances of this method which allow to separate the different colorants classes even when very diluted solutions up to  $10^{-5}$  M were analyzed. The method has been validated on a real sample micro-extract showing that this technique can be very useful for the analyses of low or trace amounts of samples with applications in the forensic, material, and conservation science field.

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## Non-invasive spectroscopic techniques for the diagnosis of *Saint Francis's Chartula*, before and after the consolidation treatments based on CaCO<sub>3</sub> nanoparticles.

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In this work, the  $\mu$ -Raman and XRF non-invasive spectroscopic techniques are applied on an important Art Work surface, as *Saint Francis's Chartula* (dated on 1224, **Figure 1**), containing the blessing of St. Francis to Friar Leo and the  $\tau$  praise, written by St. Francis on the Verna Mountain. Preliminary diagnosis reveals two main problems on the parchment support of the *Chartula*, as:

1. acidity and etching of the native parchment due to the presence of the iron-gall inks<sup>1</sup>;
2. fragments detachment (resulting in a shortening of the parchment support) and mechanical stress responsible for the visible ripples and folds, mainly due to the depletion of water and calcium<sup>2</sup> natural content.

After the diagnosis and before each restoration event, the *Chartula* was preserved for 15 days in a case with controlled temperature and humidity conditions. After that, a **2 mm** increase in size, both in height and in width, is detectable meaning that a mechanical stability has been achieved resulting in relaxation of the parchment support. The restoration and consolidation treatments were mainly performed by using the CaCO<sub>3</sub> nanoparticles, poly-dispersed in alcoholic working medium (i.e.; the isopropyl alcohol) and by the moisturizing and moistening of the parchment support. The quantitative results are shown on **Table 1**.

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**Figure 1.** *Saint Francis's Chartula*. **(a)**: the blessing of St. Francis to Friar Leo; and **(b)**: the  $\tau$  Praise.

**Table 1.** Quantitative parameters before and after the nano  $\text{CaCO}_3$  based treatments on Chartula's parchment

Inchiostro nero	ferro gallo tannico
Inchiostro rosso	cinabro
Adesivo precedente restauro	idrossipropil cellulosa
Concentrazione calcio prima del trattamento con nanocarbonato di calcio in alcol isopropilico	0.4%
Concentrazione calcio dopo il trattamento con nanocarbonato di calcio in alcol isopropilico	07 %
Larghezza massima prima della distensione	9.8 cm
Larghezza massima dopo la distensione	10.1 cm
Altezza massima prima della distensione	13.1 cm
Altezza massima dopo la distensione	13.3 cm

## Iron stains on carbonate artefacts: XPS investigation of corrosion-induced deterioration on reference stones

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As part of a research project aimed at offering a method for removing Iron stains from ancient artefacts, reference specimens made of Carrara and Travertine stones (5x5x2 cm) were placed in contact with Iron (in form of cubes, nails and salts solutions) in order to simulate corrosion-induced Iron stains, as shown in Figure 1.



**Figure 1.** Evidence of corrosion induced Iron stains on Carrara and Travertine reference stones.

The purity of Iron specimens was assessed by X-ray Fluorescence, XRF, reporting the following At% composition: Fe at  $98.6 \pm 0.2$  % plus trace amounts of Si, Ti, Cr, Mn, Si, Cu and Sn counting for the remaining percentage.

The reference stones were also characterized by Colorimetric and FTIR analyses which in turn provided indications of the variations in colour and chemical composition as a function of surface interactions with the different Iron forms, contact modalities, the ageing time, indoor or outdoor exposition and other variables reported in Experimental.

Here we report in details on the XPS analysis of the homogenized powders, scraped with a scalpel from the stained areas on specimen surfaces and specimen-iron interfaces and, also, from an area unaltered by Iron on the relevant specimens thus taken as the comparative reference kept at the same storage conditions.

XPS spectra were acquired with a SPECS "Phoibos 100-MCD5" spectrometer operating at 100W in FAT and Medium Area modality, using Al/Mg K $\alpha$  achromatic radiation. Detailed regions (channel width of 0.1 eV) were elaborated by curve-fitting, qualitatively, by referring the corrected binding energies to Fe<sub>2</sub>O<sub>3</sub> standard spectrum and literature data[1,2], see carbon, calcium, Iron and oxygen peak assignments in Table, and, quantitatively, by cross-

checking the corrected peak areas[3], not shown in Table 1, of functional groups belonging to a given compound, taking account of stoichiometric indexes.

Element/ <sub>region</sub> Assignment	Carrara indoor	Travertino indoor	Carrara outdoor	Travertino outdoor	Carrara interface	Travertino interface	Carrara reference	Travertino reference
<b>C<sub>1s</sub></b>								
Carbides	283.4	282.4	283.5	283.5	283.3	283.3	283.2	283.3
C-C	285.0	285.0	285.0	285.0	285.0	285.0	285.0	285.0
C-O	286.6	286.0	286.0	286.2	286.5	286.2	286.1	286.3
CO-OR C=O	288.7	288.5	288.7	288.4	288.6	288.3	288.7	288.6
CO <sub>3</sub> <sup>2-</sup>	290.3	290.4	290.5	290.1	290.1	290.0	290.2	290.1
<b>Ca<sub>2p</sub></b>								
Ca <sup>0</sup>	---	---	---	---	344.8	344.8	---	---
CaO	---	---	345.9	346.1	346.7	346.2	346.0	345.7
CaCO <sub>3</sub>	347.7	347.9	347.9	347.6	347.9	347.6	347.8	347.7
<b>Fe<sub>2p</sub></b>								
Fe <sup>0</sup>	---	---	---	---	---	707.8	---	---
FeO	---	---	---	---	708.3	---	---	---
Fe <sub>2</sub> O <sub>3</sub> ·xH <sub>2</sub> O	710.4	710.7	710.8	710.5	710.2	710.4	---	---
Fe <sub>2</sub> O <sub>3</sub> ·xH <sub>2</sub> O	712.1	712.0	712.6	711.8	711.6	711.4	---	---
Fe <sub>2</sub> O <sub>3</sub> ·xH <sub>2</sub> O	---	713.8	---	713.6	---	713.5	---	---
<b>O<sub>1s</sub></b>								
	530.0	530.5	530.4	530.2	530.0	529.7	530.4	530.0
	531.8	532.5	532.3	532.1	532.1	531.8	532.1	532.1

**Table 1:** Binding Energy (eV) of the main components derived by curve-fitting C1s, Ca2p, Fe2p and O1s XPS regions. BEs are corrected for surface charging by referring to C1s aliphatic carbon set at 285.0 eV.

The overall semi-quantitative analysis by XPS confirms hematite (Fe<sub>2</sub>O<sub>3</sub>) as the main components of the Iron stains on stone surfaces, as anticipated by the chromatic factors derived from Colorimetric analysis and functional groups detected by FTIR.

Moreover, the overall mass balance between the sum of the oxygen-containing groups and the total O1s area has required a variable degree of hydration and carbonate decomposition to CaO/Ca, depending on the stone type and its indoor/outdoor exposition.

More interestingly for the scope of this research, powders from the interface area (the inner Iron layers strongly adsorbed on stones) have shown the presence of Iron (II) compounds, together with Iron metallic and Iron carbides.

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## **Interference-free detection of SiO<sub>2</sub> nanoparticles in marketed food samples by AF4-ICP-MS/MS**

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The assessment of the potential risks associated to dietary exposure to inorganic nanomaterials (iNMs) requires analytical techniques that can be successfully employed in their identification and quantification in food products. Parameters such as diameter, volume, area, mass, surface charge, elemental composition, agglomeration and aggregation state play a major role in the bioavailability of iNMs in food and their potential adverse effects in humans.

Apart from human risk assessment, methods for iNMs characterization in food will be required since NMs have been included in the new EU regulation on Novel Food as potential ingredients in food, after assessment of their safety, and (official) control of the types and amounts of iNMs used will have to be implemented.

Along with titanium dioxide (TiO<sub>2</sub>) and zinc oxide, silicon dioxide (SiO<sub>2</sub>) is one of the most widely produced NMs worldwide, used in several industrial applications and found in a wide variety of food and consumers' products, including medicines, toothpastes, and cosmetics.<sup>1</sup>

The characterization of NMs in complex matrices is not a trivial task. In this respect, electron microscopy techniques (e.g. TEM, SEM) are essential for NMs imaging (e.g., investigation of morphology) but hardly provide quantitative data in complex samples, whereas inductively coupled plasma mass spectrometry (ICP-MS)-based techniques are becoming essential tools to cope with the quantitative characterization of iNMs.<sup>2</sup>

For iNMs, ICP-MS-based techniques are attractive since they are able not only to measure size and size distributions, but also to determine the chemical identity of the particles at the same time. A number of different separation techniques have been used for the separation of particles based on their size, surface, density and charge characteristics. As far as hyphenated ICP-MS-based methods are concerned, asymmetric flow field flow fractionation (AF4)-ICP-MS has been increasingly used as a versatile tool for size-based separation of inorganic nanoparticles and subsequent characterization of relevant metrics such as size and mass concentration by on-line coupling to appropriate detectors. If combined on line with multiangle light scattering (MALS), for instance, AF4 can provide direct determination of geometric diameters in flow systems. For solid samples, these techniques have to be combined with selected matrix digestion procedures, in order to extract the nanoparticles preserving their original state.

A limitation of ICP-MS-based techniques is represented by the determination of certain oxides such as SiO<sub>2</sub> that is hampered by significant analytical challenges. Sensitive and



accurate silicon determination in standard, i.e. single quadrupole, mode is precluded owing to polyatomic interferences affecting the three naturally occurring isotopes  $^{28}\text{Si}$  ( $^{14}\text{N}^{14}\text{N}^+$ ,  $^{12}\text{C}^{16}\text{O}^+$ ),  $^{29}\text{Si}$  ( $^{14}\text{N}^{15}\text{N}^+$ ,  $^{14}\text{N}^{14}\text{NH}^+$ ,  $^{13}\text{C}^{16}\text{O}^+$ ,  $^{12}\text{C}^{16}\text{OH}^+$ ), and  $^{30}\text{Si}$  ( $^{15}\text{N}^{15}\text{N}^+$ ,  $^{14}\text{N}^{15}\text{NH}^+$ ,  $^{14}\text{N}^{16}\text{O}^+$ ,  $^{13}\text{C}^{17}\text{O}^+$ ,  $^{12}\text{C}^{17}\text{OH}^+$ ), whose natural abundances are 92.2%, 4.7%, and 3.1%, respectively. The use of ICP-MS systems equipped with dynamic reaction cell (ICP-DRC-MS) or tandem mass spectrometry (ICP-MS/MS) does represent a viable solution for the interference-free quantitative determination of  $\text{SiO}_2$  in different sample types.<sup>3-4</sup>

Sample preparation and detection methods for the determination of  $\text{SiO}_2$  nanoparticles in complex matrices will be presented with focus on state-of-the-art mass spectrometric techniques and AF4 combined on-line with optical detectors (MALS, UV) for size determination, and elemental detection by ICP-MS/MS. The approaches developed to overcome the analytical challenges associated with the determination of  $\text{SiO}_2$  in food samples bought at retail and containing synthetic amorphous silica (E551) as food additive will be discussed.

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## Targeted and untargeted alkaloids profiling of alpine flora using high resolution mass spectrometry (Q-Orbitrap).

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Alkaloids (ALKs) are an extremely varied group of natural, nitrogen-containing, and basic organic compounds. Their biological activity makes them very attractive for pharmaceutical studies and clinical trials, and currently over ten thousand ALKs have been isolated and identified from natural sources. ALKs have been classified into three principal classes depending on precursors and final molecular structures: atypical (non-heterocyclic compounds, sometimes called 'proto-ALKs' or biological amines), typical (heterocyclic compounds further classified into: pyrrole, pyrrolidine, tropane, pyrrolizidine, piperidine, quinoline, isoquinoline, aporphine, quinolizidine, indole, indolizidine, pyridine, imidazole, and purine groups), and pseudo-ALKs (basic compounds, not derived from amino acids). Usually considered simply waste products of plant metabolic processes [1], the very differentiated chemical structure suggests that they play various specific biological roles, from plant protection against pathogen and herbivore attacks [2] to scavenger activity against of reactive oxygen radicals [3].

In this work we propose a new method that combining the SPE-on line sample pretreatment with the high resolution mass analysis (Q-Orbitrap) allowed an extensive ALK characterization of 80 mountain herbs from the Italian alpine flora. The on-line concentration/purification was performed with a SolEx HRP spe cartridge, while the chromatographic separation with a Raptor Biphenyl analytical column, managing the water/0,1% formic acid/5mM ammonium acetate – methanol:acetonitrile (95:5 v/v)/0,1% formic acid/5mM ammonium acetate gradient elution in 32 minutes from 30% to 100% of organic solvent. The mass spectrometer was operated in positive ion mode using the following parameters: sheath gas flow rate set at 30 arbitrary units; aux gas flow rate at 10 arbitrary units; spray voltage at 3.5 kV; capillary temperature at 330 °C; aux gas heater temperature at 300 °C; Mass spectra were acquired in full MS-data dependent MS/MS analysis (full MS–dd MS/MS) at mass resolving power of 140.000.

Sample extract was prepared mincing 2.5 g of fresh or frozen (-20°C) herbal sample with 20 mL of water/methanol/formic acid (94.5:94.5:1) solution. The mixture was sonicated (10 minutes), extracted overnight under rotary agitation (12 hours), and centrifuged (4100 rpm). The supernatant was filtered 0.45 µm and analyzed.

35 ALKs were quantified in reference to the pure analytical standards. The method response was linear up to concentration of 1000/3000 µg L<sup>-1</sup> with a R<sup>2</sup> at least of 0,99 and limits of detection were generally low 0.05-10 µg L<sup>-1</sup>. Relative errors %, used to define method accuracy, was less than 10% for over 70% of analytes, and the precision (RSD %) was

generally < 10% in all the quantitation range. 49 ALKs were tentatively confirmed, concerning chromatographic retention time and fragmentation profile, analyzing the extracts of herbs of already well documented composition (*Arnica montana*, *Lobelia inflata*, *Gelsemium sempervirens*, *Ranunculus montanus*, *Senecio vulgaris*, *Datura stramonium*, *Hyoscyamus niger*, and *Solanum nigrum*). Other 200 ALKs were identified using a database built from literature information regarding exact masses and isotopic patterns.

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## Photocatalysis of Pollutants' degradation using TiO<sub>2</sub> Coated Glass

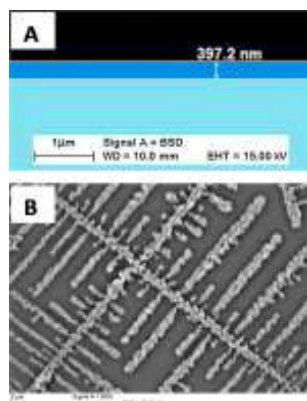
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Advanced oxidation processes (AOPs) have been proved as an innovative and promising alternative route for the treatment of wastewater containing recalcitrant organic compounds such as pesticides, pharmaceuticals, surfactants, colouring matters and endocrine disrupting chemicals. Some of these compounds pose severe problems in biological treatment systems due to their resistance to biodegradation, and often exert toxic effects on microbial processes [1]. Among AOPs technologies, heterogeneous photocatalysis with semiconductors was the most popular and effective widely employed method for water purification and wastewater treatment [2]. This study examines the photocatalytic activity of titanium dioxide (TiO<sub>2</sub>) towards removal of persistent organic pollutants (POPs) from water. Model compounds including a widely used analgesic and anti-inflammatory drug, ibuprofen, along with mepanipyrim, which is a common fungicide frequently used in the agricultural activities have been selected as case study. Two experiments were carried out using TiO<sub>2</sub> as (i) dispersed powder; (ii) TiO<sub>2</sub> immobilized on the surface of a commercial coated glass. The scanning electron analysis for the TiO<sub>2</sub> coated active glass was also accomplished (Fig.1). A cooled solar simulator furnished with a xenon lamp 1,500 W total power, 500 W/m<sup>2</sup> irradiance, in the wavelength range 290-800 nm was used for sample irradiation at 25°C constant temperature.

Kinetics of each photoreaction was determined, and the identification of the photoproducts was performed using liquid chromatography coupled with Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (LC-FTICR MS). The overall results suggest that active thin layer of TiO<sub>2</sub> immobilized on glass surface can avoid the recovery problems related to the use of TiO<sub>2</sub> powder in heterogeneous photocatalysis and may be a promising tool towards protecting the environment from emerging contaminants such as ibuprofen and mepanipyrim [3].



**Figure 1.** (A) SEM reconstructed and coloured micrograph of the Pilkington Active™ Blue glass cross section showing the TiO<sub>2</sub> layer immobilized on the glass surface; (B) SEM original micrograph of the Blue glass surface showing the fine-toothcomb of TiO<sub>2</sub> coating.

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## **Bimetal Cu/Ag nanoparticles synthesized by laser ablation in aqueous and organic solution: process optimization and materials characterization**

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Bimetal nanoparticles (NPs) offer unique catalytic, electrochemical and optical properties, compared to single-metal NPs<sup>1-2</sup>. Particularly, Cu/Ag hybrid structures are attracting increasing interest in the scientific community, due to the combination of the antimicrobial activity exerted by both metals. Among all methods for preparing bimetal NPs, laser ablation synthesis in solution<sup>3</sup> (LASiS) is a simple, rapid and green approach. Based on our previous work carried out on CuNPs, in this study Cu/Ag bimetal nanoparticles were synthesized by femtosecond laser ablation in presence of Chitosan (CS) as stabilizing agent, in 0.1%<sub>v/v</sub> acetic acid (HAc) solution<sup>4</sup>. Unlike what previously reported, where the ablation process took place in a static environment, this time it was carried out in a flow-cell system. This set-up allowed us to obtain higher yields and surprising morphological control. Cu and Ag target were alternatively selected as first ablated metal, followed by the ablation of second metal directly into primary colloidal solution. In a first approach, CS was used as ultimate capping agent, at its optimal working concentration of 1 g/L<sup>4</sup>. Thanks to their hypothesized bioactivity and associated low toxicity for humans<sup>5</sup>, these hybrid NPs could be used in medicine, cosmetics or in food industry<sup>6-7</sup>. Particularly, for the production of bioactive food packaging, Cu/Ag bimetal nanoparticles could be dispersed into a polymer matrix, in order to improve polymer properties and to impart it antimicrobial capabilities. For this purpose, being most of the industrial polymers just soluble in organic solvents, LASiS synthesis of bimetal NPs was also performed in pure acetone. All mono- and bimetal NPs, obtained under different experimental conditions (different flow rates, composition of the liquid medium, ablation parameters, etc.), were characterized by transmission electron microscopy (TEM), UV-Vis, and X-ray photoelectron spectroscopy, aiming at evaluating their morphology and chemical composition.

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## Characterization of brass alloys aged at open circuit potential in neutral solutions

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Since centuries, brass (Cu-Zn alloys) are used as material for wind instruments due to the ease of manufacturing, their high corrosion resistance and their good acoustic properties [1]. Contemporary musical practice intends more and more to play original instruments in concerts, following the “historically informed performance practice” (HIP). When historical instruments get regularly played, the main concern of museums and conservators is corrosion of the brass instruments due to the high humidity inside the instruments formed during playing [2] that might damage the artefacts on long-term. The aim of the multi-disciplinary project was to get an insight in the corrosion of brass used for the wind instruments. The project will provide the conservators the necessary information on the corrosion rates that might be expected inside the instruments and to check if preventative methods (e.g. drying the instruments with warm air) are effective.

The actual corrosion state inside the ancient instruments can be determined with non-destructive and portable techniques. In previous works [1, 3] a small electrochemical sensor was developed and used to assess corrosion potentials (OCP) and corrosion rate ( $i_{\text{corr}}$ ) on tuning slides of different brass instruments before and after being played. Full interpretation of the results requires knowledge of the surface state at the point of measurement inside the historical instruments [1] – thus a clear relation between electrochemical and surface analytical information is needed.

*The scope of this work was to establish this relation combining electrochemical and surface analytical techniques.* Model brass alloys with 18 to 37% of zinc were exposed for 1, 3 and 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, more aggressive, an artificial saliva solution [4]. The ageing process was investigated with electrochemical measurements such as open circuit potential (OCP), linear polarization resistance ( $R_p$ ), potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). The results showed that corrosion rates were, as expected, initially higher in the artificial saliva compared to the phosphate buffer solution. With prolonged exposure (ageing) to the artificial saliva the OCP values became more positive and the corrosion rate decreased strongly.

X-ray photoelectron spectroscopy (XPS) and X-ray Auger electron spectroscopy (XAES) surface analytical techniques were used to characterize the surface state of the same brass samples before and after the contact to the solutions. X-ray photoelectron spectroscopy



(XPS) is particularly well suited for characterizing cultural heritage artefacts because it is non-destructive, has excellent surface sensitivity in the nanometre depth range, can identify the elements and their chemical state. For brass this is however more complex. As it is well known both copper and zinc do not show a chemical shift in the XPS Cu2p and Zn2p signals, distinction between the metallic and oxidized state is not possible [5]. Thus first an analytical method based on the X-ray excited Auger signals CuLMM and ZnLMM to identify the chemical state of copper and zinc was developed. Based on standards where the XPS Me2p and XAES MeLMM spectra were measured, an analytical procedure was developed that allows the quantitative analysis of thin-layered systems on brass alloys [5].

Based on the chemical state plots of copper and zinc the different surface state of brass can be clearly distinguished: mechanically polished alloys showed a thin ZnO and Cu<sub>2</sub>O film on the surface, “as received” samples of the model brass alloys showed natural cupric oxide and hydroxides and ZnO layers while ancient artefacts exhibited the presence of a thick altered layers mainly constituted by oxides, hydroxides and carbonates. This different surface state allowed us to partially explain the results of the electrochemical measurements carried out inside the instruments [1]. In this work, prolonged exposure to the artificial saliva solution formed a thick surface film composed of CuSCN and Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, in phosphate buffer solution pH 7 only thin films mainly Cu<sub>2</sub>O, CuO and Zn(OH)<sub>2</sub> 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.

Surface analytical (XPS and XAES) and electrochemical experiments on laboratory samples with known surface state are on going in order to create the necessary basis to correlate the results of electrochemical measurements inside the historical instruments to the otherwise not directly accessible surface state.

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# Poster presentations

## Untargeted high resolution mass analytical method (SPE-LC- Q-Orbitrap) for glycosylated simple phenol profiling in natural food matrices

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Phenolic compounds, ubiquitous in plants, constitute a significant contribution to the intake of natural antioxidants in the human diet, and raise great interest due to their potential beneficial health effects<sup>1</sup>. Their antioxidant activity depends on the number and arrangement of the hydroxyl groups on the aromatic ring<sup>2,3</sup>. In food, antioxidants act as free radical scavengers (FRS), decreasing rancidity development, retarding the formation of toxic oxidation products, and extending the natural products' shelf-life<sup>1</sup>. The health protective effects of free simple phenols, that have the simplest chemical structure among phenolic compounds, have been ascribed to their antioxidant, antimutagenic, anticarcinogenic, antiinflammatory, antimicrobial, and other biological properties<sup>4</sup>. In plants they are usually present both in free and glycosidically bound forms. The latter represent a natural source of free phenolic compounds, that can be freed by hydrolysis to the corresponding free forms during food processing or fermentation, and have the same antioxidant behaviour of the corresponding free and esterified forms<sup>5</sup>.

Combining an automatic on-line SPE clean-up for reducing matrix interferences with ultra-high liquid chromatography coupled with hybrid quadrupole-high resolution mass spectrometry (Q-Orbitrap), a new untargeted approach was developed, offering new opportunities for a detailed description of the bound phenol profiles in different commodities. On-line SPE clean-up was performed by loading 2 µl of sample on a HyperSep<sup>TM</sup> Retain PEP spe cartridge (3.0 mm x 10 mm, 40-60 µm, Thermo Scientific, Sunnyvale, CA, USA), with deionized water at a flow rate of 0.250 ml min<sup>-1</sup>. The chromatographic separation was performed with an Acquity UPLC BEH C18 analytical column (2.1 mm x 100 mm, 1.7 µm particle size; Waters, Milford, MA, USA) at the flow rate of 0.400 ml min<sup>-1</sup>, managing a water-acetonitrile gradient from 5% to 100% of organic solvent. Identification and quantification of glycosylated phenolic compounds were performed using a Q-Exactive<sup>TM</sup> hybrid quadrupole-orbitrap mass spectrometer (HQ-OMS, Thermo Scientific, Bremen, Germany) equipped with heated electrospray ionization (HESI-II). Mass spectra were acquired in full MS-data dependent MS/MS analysis at mass resolving power of 140.000, in negative ion mode.

The untargeted approach, validated using synthesized glycosidic precursors, was aimed to characterize the phenolic composition of different natural matrices (cocoa, vanilla extracts, wine and food tannins), and to tentatively identify the glycosylated precursors in the forms of -

hexoside, -pentoside, -hexoside-hexoside, -hexoside-pentoside, -pentoside-hexoside and -pentoside-pentoside.

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## **A surface plasmon resonance sensor based on molecularly imprinted polymer for transformer oil control**

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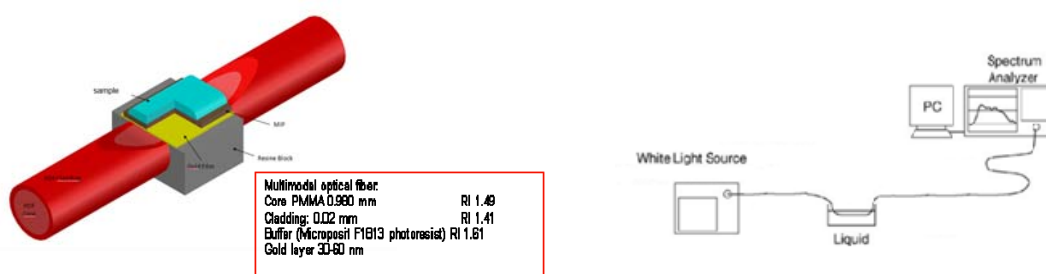
Dibenzyl disulfide (DBDS) is an important analyte in the control of transformer oil since it is commonly added to the transformer oils as an antioxidant. At the same time it is responsible for the corrosive properties of the oil, even at relatively low concentration. The determination of its level in transformer oils is of paramount importance for diagnostic purposes to monitor the “health status” of the transformer [1]. To this aim, analytical methods based on chemo-sensors appear to be very helpful for making in situ or even on line controls.

Surface plasmon resonance (SPR) is a common tool for surface interaction analysis widely used as a detection method in bio-sensors too. The method is able to evaluate small refractive index changes at the interface between a metal and a dielectric medium, usually determined by angular or spectral interrogation, based on Kretschman configuration with a prism as waveguide. This requires a bulky and expensive instrumentation, hardly suitable for out-of-the-lab application. However recently new optical platforms have been proposed, based on plastic optical fibers as waveguide [2-4], which are able to detect small refractive index variations of the dielectric in contact. A schematic view of the platform, and of the experimental set-up is reported in Fig. 1. It is evident that only the spectral interrogation can be used in the case of optical fiber, i.e. the variation of the refractive index of the dielectric is measured as a shift of the plasmon resonance wavelength. On the other hand, the light source is a small and cheap halogen lamp (Model no. HL-2000-LL, manufactured by Ocean Optics), and so is the spectrum analyzer (Ocean Optics USB2000+VIS-NIR-ES spectrometer). It has been demonstrated that the platform in Fig 1 responds with a sufficient sensitivity in a refractive index range from about 1.33 to 1.42 RIU [3].

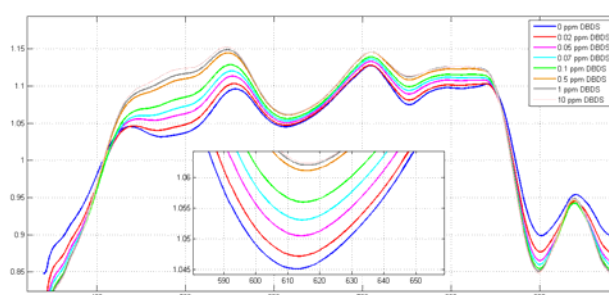
Moreover the optical platform has a flat surface, which is particularly suitable for the application of a metal layer (gold in the present case). This can be simply derivatized with a proper receptor, in order to obtain the selective sensing device.

In the sensor here proposed a molecular imprinted polymer (MIP) is used as a synthetic receptor, instead of the most usual bio receptors. The formation of a monolithic MIP layer over the flat surface is easily and reproducibly done. MIPs present a number of favorable aspects for sensing in comparison to bioreceptors, including a better stability out of the native environment, a better reproducibility and a lower cost. The MIP acts as a specific and strong receptor, and at the same time it is the dielectric medium in contact with the metal layer. Upon combination of the analyte with the sites on MIP the refractive index of the

polymer changes, producing a variation of the plasmon resonance wavelength, as shown in Fig.2 (transmission spectra), in which the effect of the combination of the specific molecule of interest, dibenzyl disulfide (DBDS), with the corresponding MIP is reported. It is evident that the refractive index of the MIP here considered (methacrylic acid-divinylbenzene copolymer) is suitable for the proposed platform, since the resonance wavelength can be easily detected [5]. The effect of increasing concentrations of DBDS is clearly seen: there is a shift of the resonance wavelength to the higher wavelengths at increasing concentration of DBDS. The effect is seen in the concentration range from  $2 \cdot 10^{-7}$  M to  $4 \cdot 10^{-6}$  M. It is not linear, but it can be fitted to the Hill model, corresponding to a combination of DBDS to its specific imprinted sites in the polymer. It has been found that the SPR wavelength in the proposed configuration depends on the DBDS concentration in mineral transformer oil, which is the matrix of interest in the present research project.



**Figure 1-** Schematic cross-section of the sensor, showing the core and the cladding of the optical fiber and experimental set-up.



**Figure 2-** Transmission spectra of a DBDS-MIP sensor at different concentrations of DBDS in mineral transmission oil (Nitro Lybra). Thickness of the gold layer: 30 nm.

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## **Electrosynthesis and characterization of composite material platinum nanoparticles/polypyrrole nanowires for sensing applications**

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Composite materials present remarkable potential applications as they combine distinct properties of individual components within a single matrix with enhanced or new properties. Carbon nanotubes, graphene and conductive polymers are widely used for the manufacturing of composite materials for their properties, such as good electric conductivity, flexibility, convenient processing and high specific surface area. In particular, great attention is devoted to the design of composite materials consisting of a mixture of nanoparticles (NPs) and organic phases due to specific nanoparticle properties, which may be exhibited to the nanoscale but are not typical of the corresponding bulk material. These include enhanced mass transport, high active surface area, electrocatalytic activity and unique optical properties. Combining properties of the individual components make composite materials ideal candidates for application in catalysis, separation, sorption, solar cells, supercapacitors, fuel cells and for the fabrication of sensing devices<sup>1</sup>.

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 based on formation of hydroxyl radicals and nanobubbles of dioxygen due to water oxidation<sup>2</sup>, and Pt-NPs are electrodeposited by exploiting both Cyclic Voltammetry (CV)<sup>3</sup> and Potential Step techniques (PS)<sup>4</sup>. In particular, for each method, a systematic investigation of experimental conditions potentially influencing PtNPs size, distribution, morphology and electroactivity (i.e. number of scans/scan rate and applied potential/potential step for CV and PS, respectively) have been performed. Electrochemical, morphological and chemical characterizations of PPy-NWs/PtNPs samples have been performed. CV experiments provided evidence about PtNP deposition and electroactivity. 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 thus representing a useful tool for clarifying platinum deposition mechanism. Moreover, also an estimation of the amount of deposited platinum was obtained by atomic ratio Pt 4f/N 1s. XPS data, along with electrochemical and morphological characterization provide valuable information for identifying optimal conditions for preparing PPy-NWs/PtNPs material to be used in sensing applications, as hydrogen peroxide electrochemical detection.

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## Spectroscopic and electrochemical characterization of Nickel-Cobalt/Graphene/Polyvinyl alcohol nanocomposites

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The nickel and cobalt oxides exhibit large pseudocapacitance activity, good electrocatalytic performance, electrochromic and anti-corrosion properties [1-4]. Carbon nanomaterials, and in particular graphene (GO) structures are considered attractive electrode substrates due to their superior electrical conductivity, high theoretical surface area and good electrochemical stability [5]. In this respect, graphene-based structures containing metal oxides makes these composite materials as excellent candidates for the preparation of electrochemical devices with improved electrochemical properties. Thus, these composite materials have been successfully synthesized and characterized [6].

Herein, we report a codeposition of fine Ni + Co particles on graphene platelets dispersed into polyvinyl alcohol polymer (PVA) by cycling the potentials between – 0.5 V and 0.2 V vs SCE. The base of polyvinyl alcohol film (PVA) structured with particles of oxidized graphene (GO) was prepared through a "casting" process. The composite electrode was defined as PVA/GO/Co-Ni and characterized using voltammetric techniques, SEM and XPS spectroscopic techniques.

The surface morphology of the composite material, was examined using the scanning electron microscopy (SEM) technique, comparing the structures of PVA, PVA/GO, PVA/GO/Ni and PVA/GO/Co-Ni before and after electrochemical treatments in alkaline medium (NaOH 0.1 M). The images show that the graphene platelets are randomly oriented in the PVA matrix and the Co-Ni particles are efficiently dispersed through a 3D (three-dimensional) configuration. The metal deposit shows globular disordered structures having an average diameter comprised between 80 and 150 nm.

The surface chemical speciation of the composite was evaluated using the XPS technique, through a comparative analysis of C1s, Ni2p3/2, Co2p3/2 e O1s signals. The atomic ratio Co:Ni obtained from Co2p3/2:Ni2p3/2 signals, has allowed to establish an average chemical composition:  $\text{Co}_{84\pm5}\text{Ni}_{16\pm5}$  of the composite, confirming a substantial *anomalous codeposition* of the metals within the PVA/GO electrode substrate. Also, the O1s:(Co2p+Ni2p) atomic ratio and the detailed analysis of the Ni2p3/2 and Co2p3/2 XPS signals, reveals the dominant presence on the electrode surface of metal oxyhydroxide species at high oxidation state (CoOOH, NiOOH, CoO<sub>2</sub>, etc.).

The resulting PVA/GO/Co-Ni composite, tested during prolonged charge/discharge cycles in alkaline medium, shows promising capacitance properties if compared with the cobaltite, or PVA/GO substrate electrode.

In addition, the PVA/GO/Co-Ni composite electrode was characterized as sensing probe for the electrocatalytic oxidation of some molecules such as: methanol, formic acid, sorbitol and glucose.

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## Fourier Transform Infrared Spectroscopy in the leather quality control: the project LIFETAN: and eco friendly tanning cycle <sup>1</sup>

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LIFETAN project is aimed at demonstrating 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 with the traditional one. Six new tanning formulations with natural products will be proposed and tested, characterized by higher biodegradability 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<sup>-1</sup> absorbance ratio to evaluate the collagen cross linking) and the analysis of the single components found by peak fitting (conformational analysis) <sup>2,3</sup>.

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## **Halloysite Nanotubes (HNTs) and Kaolinite (Kao): Fourier Transform Infrared Spectroscopy (FT-IR) study of the interactions with bovine serum albumin (BSA)**

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During the last few decades, materials based on nanoclays have attracted large interest because their properties and morphologies may be tuned. Within this field, halloysite nanotubes (HNTs) are newly emerging clays with unique features and appealing perspectives. In particular, HNTs are considered an ideal material for biotechnological and medical applications.

The study of the interaction between nanoparticles/nanotubes and proteins is important because the modifications that biological molecules undergo upon their interaction with nanostructured materials may alter their function.

For example, 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 the present 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 have clearly shown that the conformational changes of BSA depend on protein concentration, clay morphology and clay/protein ratio. The surface curvature radius seems to have a big role in the final protein conformation. Both curved nanoscale surface of HNTs and the flat morphology of Kao deeply interfere on the  $\alpha/\beta$  transitions of BSA. This determines also the percentage of protein adsorbed on the clay surface.

## **Loading of BSA, $\alpha$ -Lac and $\beta$ -Lg into Halloysite nanotubes: study of protein conformation by Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy and thermogravimetric analysis (TGA)**

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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 halloysite 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 (lumen) surface. Aluminium and silicon oxides have different ionization properties and surface charge. This is evident from zeta-potentials of their colloids in water. 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 halloysite nanoscale lumen. 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 ( $\alpha$ -Lac) and beta lactoglobulin ( $\beta$ -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.

## Combined LC-MS/MS and Molecular Networking approach to discover novel metabolites

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Cyanobacteria have a long history of ecological and health impacts. This unique class of photosynthetic microorganisms can generally survive in nearly all phototrophic aquatic environments, including recreational water bodies, fisheries, and reservoirs. In the last two decades, worldwide attention has been given to the ecological effects of cyanobacteria and to their production of secondary metabolites. They represent a not yet fully explored source of novel lead compounds for drug discovery, such as the dolastatins, cryptophycins, and curacins, that have in turn inspired the development of synthetic analogues with improved bioactivity and pharmacokinetics.

However, cyanobacteria growing in freshwater and marine recreational areas may have a strongly negative impact on human health. Some species can form extensive blooms, and there is evidence that these are increasing during recent decades due to nutrient enrichment, especially phosphorus. Many cyanobacteria produce toxic secondary metabolites (cyanotoxins) with differing effects on health, ranging from mild skin irritations to severe illness.

We have initiated a worldwide program to study their chemistry and biochemistry. In this communication, I wish to report recent results from our study on the cyanotoxins obtained from a freshwater cyanobacterial collection at Green Lake, Seattle during a cyanobacterial harmful algal bloom (cyanoHAB) in the summer of 2014<sup>1</sup>. Our study was based on a new approach based on molecular networking analysis of liquid chromatography tandem mass spectrometry (LC-MS/MS) data. In this communication the new approach will be described highlighting the usefulness of combined LC-MS/MS and Molecular Networking to discover novel metabolites.

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## A general approach to the immobilization of glyco-enzymes acting in cascade inside calcium alginate beads

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In this work an enzyme encapsulation general approach, based on the use of calcium alginate hydrogels, is reported.

Alginate is an anionic polymer, widely used in medicine, pharmaceutical and biotechnology, that can be gelled with multivalent cations under gentle conditions. When alginate is dripped into a bath containing a Ca<sup>++</sup> solution, the cations diffuse from the continuous phase to the interior of the alginate droplets and form hydrogel beads of few mm of diameter, used for the entrapment of sensitive materials (Figure 1).

The entrapment of enzymes in alginate beads suffers some disadvantages, like as low enzyme loading efficiency with reduction of the immobilization yields and reusability, related to the enzyme leakage from the large beads pores.

We used alginate beads to entrap, as model system, three glycoenzymes (trehalase, glucose oxidase and horseradish peroxidase) acting in series. Leakage of entrapped enzymes after gelation has been avoided by exploiting the enzymes aggregation induced by the concanavalin A.

The aggregation process has been monitored by dynamic light scattering technique, while both enzyme encapsulation efficiency and leakage have spectrophotometrically been quantified. Obtained data show an encapsulation efficiency above 95% and a negligible leakage from the beads when enzyme aggregates are larger than 300 nm. Operational stability of “as prepared” beads has been largely improved by a coating of alternated shells of polycation poly(diallyldimethylammonium chloride) and of alginate.

As a test for the effectiveness of the overall procedure, analytical bio-assays exploiting the enzyme containing beads have been developed for the optical determination of glucose and trehalose<sup>1</sup>.

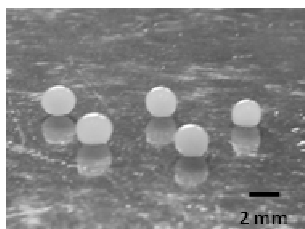


Figure 1.

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## **XPS characterization of mussel adhesive protein inspired coatings: screening of optimal conditions for facile biomolecules conjugation**

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Among the available surface functionalization methods performed in the wet state, only very few allow for the formation of a functional and uniform coating on a large variety of substrates in a single step. Among these, the deposition of polydopamine films from a basic solution of dopamine has emerged as a simple and effective way to form multifunctional polymer coatings on virtually any substrates [1]. Inspired by the composition of adhesive proteins in mussels, dopamine self-polymerization has been used to form thin, surface-adherent polydopamine films onto a wide range of organic and inorganic materials, including noble metals, oxides, polymers, semiconductors and ceramics. Although polydopamine deposition mechanism as well as its chemical composition are not precisely known, catechol and quinone functional groups are believed to be present in the polydopamine coating, the latter of which are capable of covalent coupling to nucleophiles. The reactivity of polydopamine films towards amine and thiol groups has been ascribed to reactions between nucleophiles and polydopamine surface and has been exploited to covalently immobilize biomolecules onto its surfaces [2, 3].

In the present study, polydopamine films have been deposited on gold surfaces from stirred basic solutions (pH 8.5) by autoxidation of dopamine at different time intervals (namely, 1, 3, 5, 8, 18, and 24 hours). On the basis of the reported effect of oxygen in increasing the reaction kinetics of alkaline dopamine oxidation [4], polydopamine deposition has been performed in the same conditions under a pure oxygen environment. Moreover, for a comparison, polydopamine coatings have been prepared also by exploiting chemical dopamine oxidation in the presence of a strong oxidizing agent for the same time intervals and electrochemical oxidation by cyclic voltammetry. As prepared samples have been investigated by X-Ray Photoelectron Spectroscopy (XPS) with the aim to identify chemical functionalities and to estimate film thickness as a function of deposition time, under each tested conditions. Comparison of XPS data about elemental composition, distribution of functional groups and thickness of polydopamine coatings provided valuable information for identifying more suitable polydopamine films for biomolecules anchoring, thus further advancing the use of polydopamine as a modification layer for several applications.

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## Characterization of new naturalised dyes by FTIR and atomic spectrometry

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Naturalised dyes (NDs) are a new class of dyes which can be synthetically achieved by the union of a molecule of a chromophore with a molecule of lactose through a chemical coupling (amide or ester). In consideration of their potential role in the improvement of eco sustainability of industrial dyeing processes, NDs are currently investigated in the Life EU project "BioNaD", which is focused on leather industry [1].

The evidence which have been collected during the development of BioNaD project confirms that NDs can be obtained as pure, water soluble products. NDs don't need the use of additives as for commercial dyes (salts, surfactants, dispersants, paraffins) and they are biodegradable compounds (by selected bacteria and /or fungi). The use of NDs results in lower BOD and COD values (about 50%), in a reduced water consumption. Furthermore the production of NDs allows the reuse of lactose, a waste product of dairy industry.

Standard ISO tests demonstrated that the quality of leather dyed with NDs is comparable with that obtained by commercial dyes (chromophore + additives). Last, but not least, the NDs can be employed in tanneries without any technical modification of dyeing facilities or dyeing procedure in terms of dye concentration, temperature and processing time.

During the development of BioNaD project more evidence have been collected which discloses unforeseen properties of NDs.

First, the superior capacity of penetration of NDs inside the leather with respect to commercial dyes. Dedicated study, performed by FTIR and calorimetry, indicated different types of interaction of NDs and commercial dyes with collagen. In particular NDs interact with collagen through chemical reactions and hydrogen bonding. Both interactions involved the lactose portion of the ND molecule. In commercial dyes the interaction of chromophore with collagen are of electrostatic in nature [2].

Second, NDs present a lower concentration level metals and other trace elements respect to commercial dyes. This evidence has been collected by selecting four different colors (yellow, orange, blue, red) and different class of dyes: (i) commercial dyes, which contains the commercial chromophore plus additives; (ii) the commercial chromophore; (iii) the purified chromophore and, (iv) the NDs. A total of 19 elements were selected and determined by ICP-OES (Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Tl, V e Zn) after microwave acid digestion. Mercury has been determined by AAS using a direct mercury analyser.

The results indicated that the total element concentration decreased in the order:

Commercial Dyes > Commercial Chromophore ≥ Naturalised Dyes > Purified Chromophore

The total element concentration of NDs is 2-10 folds lower than in commercial dyes. For Hg NDs present concentration that are 20-30 fold lower than in commercial dyes.

Form the comparison of the concentration of the elements in the four different classes of dyes it appears evident that the higher contamination of commercial dyes arises from the additives, which are present in commercial dyes at elevated concentrations (50-70%). This is a further, potential advantage arising from the use of NDs in leather dyeing process.

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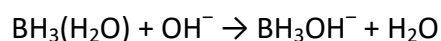
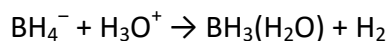
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## Vapor generation for trace element determination. Focus on Cadmium

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Chemical vapor generation (CVG) of cadmium has been investigated by continuous flow reaction system coupled either with quartz tube (QTA) or mini diffusion flame (MDF) as atomizers and atomic absorption spectrometry (AAS) or with ion coupled plasma optical emission spectrometry (ICP-OES). Experimental evidence collected in the present study indicates that  $\text{BH}_3\text{OH}^-$  is the most likely effective species in the generation of volatile Cd species. It can be synthesized on-line by quenching the acid hydrolysis of  $\text{BH}_4^-$  by NaOH, according the following reactions [1]



The most interesting effect has been obtained for QTA-AAS, in the range 1-5  $\mu\text{g L}^{-1}$  Cd. In this system, the use of  $\text{BH}_3\text{OH}^-$  in alkaline conditions increases the sensitivity of about a factor 2.2 with respect to  $\text{BH}_4^-$ , indicating an improved generation efficiency. Dissolved oxygen has been proved to severely interfere in volatile Cd species generation, as flushing argon into reaction solutions resulted in a sensitivity improvement of about 8 fold and 6 fold by using  $\text{BH}_4^-$  and  $\text{BH}_3\text{OH}^-$  as reductants, respectively. Oxygen gas added between gas-liquid separator and atomizer hardly affects the sensitivity, indicating that the oxygen interferes mainly in the liquid phase, during the generation step of volatile Cd species. The use of  $\text{BH}_3\text{OH}^-$  under oxygen free conditions resulted about 13 fold improved LODs (about 10  $\text{ng L}^{-1}$ , 3s). Signal enhancement by oxygen free conditions varies with generation condition, being lower with ICP-OES and MDF/AAS at higher Cd levels.

Calibration curves obtained either by reduction with  $\text{BH}_4^-$  or  $\text{BH}_3\text{OH}^-$  are affected by rollover at Cd concentration of 50-100  $\mu\text{g L}^{-1}$ , depending on reaction conditions. This effect has been accompanied by double peaks formation, and can be addressed to self interference effect due to dispersed solid phase formed by Cd atoms aggregation.

Chemical vapor generation (CVG) of cadmium by reduction with  $\text{BH}_3\text{OH}^-$  suffers from interferences as the generation efficiency drops down in the presence of 1  $\text{mg L}^{-1}$  Fe(III), Ni(II) and Co(II), 0.05  $\text{mg L}^{-1}$  Cu(II) and in real samples: masking agents usually employed also as signal enhancers[2], such as thiourea/Ni(II), slightly control interferences, with 10% enhancement; thiourea content > 0.1  $\text{g L}^{-1}$  resulted in a marked signal depression.

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## **Innovative natural defatting agents: FTIR study of the interaction with leather proteins and monitoring of the environmental impact<sup>1</sup>**

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Leather manufacturing combines several working phases that transform waste materials of the cattle industry such as animal skins (or hides) 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 that are 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 have used Attenuated Total Reflectance- Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Thermogravimetric Analysis (TGA) for the study of natural defatting agents/leather protein interactions at molecular level.

The monitoring of the environmental impact of defatting effluents from the use of new formulations was carried out through the metal analysis performed with Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Direct Mercury Analyzer (DMA).

To comparison, also some commercial products were analyzed.

We have demonstrated the effective capability of some of the developed natural compounds to replace the commercial products and reduce the environmental impact of defatting effluents.

1. Life + EU Project ENV/IT/000470 "ECODEFATTING"

## Characterization of sheep skin by FT-IR spectroscopy, after the degreasing stage with formulations containing lactose derivatives<sup>1</sup>

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Project Life+ 13 ENV/IT/000470-Ecodefatting aims at demonstrating the use of innovative defatting agents, to remove the fat content in animal hides before these are tanned. The degreasing phase within the tannery processing cycle is quite important, because the removal of fat is crucial for the next tanning phase. If the fat is not taken away efficiently, the tanning agents cannot work properly within the molecular structure of the leather, leading to poor quality material susceptible to mechanical degradation over time. On the other hand, if the removed fat is too much, the leather becomes stiff and fragile, leading to tears and rips. In the last decades the defatting of animal hides has moved from the use of chlorinated paraffins and alkyl phenol derivatives, because of their environmental impact and hazards to human health<sup>2</sup>. At present, ethoxylated long chain alcohols<sup>3</sup> are the degreasing agents of choice, but many such products of different quality are available on the market. In addition, commercial degreasing agents contain ethoxylated vegetable oils and sugars, rendering the whole formulation complex and difficult for waste management when effluents are discharged. The Ecodefatting project introduces new defatting agents based on the elaboration of the sugar lactose, a byproduct of the dairy industry<sup>4</sup>. Defatting tests were carried out on sheep skins samples, coming from the pickling stage of the tanning cycle. The samples were characterized through physical tests and by FT-IR spectroscopy in the ATR mode and using a TSG detector. The main protein peaks of the amide backbone structure were identified in the region of Amide I for the C=O stretching (1700-1600 cm<sup>-1</sup>) and Amide II for the in-plane N-H bending and the Csp<sup>2</sup>-N stretching (1575-1480 cm<sup>-1</sup>)<sup>5</sup>. Peaks associated to residual fat were in the region 3000-2750 cm<sup>-1</sup> (Csp<sup>3</sup>-H) (Area 1) and 1770-1700 cm<sup>-1</sup> (C=O) (Area 2).

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## UV-photochemical vapor generation at trace level of selenium species with a germicidal mercury lamp and low organic acid concentration

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Nowadays photochemical vapor generation (photo-CVG) is a good competitor of conventional chemical vapor generation for the determination of hydride-forming elements, transition metals and non-metals. Photo-CVG is based on absorption of ultraviolet (UV) radiation by a low molecular weight organic acid, which generates radicals necessary to the vapor generation process.[1][2]

Our study is focalized on the application of this technique to selenium inorganic species (mainly Se(IV)) using a very simple and cheaply photochemical generation system consisting of a commercially available germicidal UV lamp and formic acid at very low concentration (0.1-0.2 % w/w). Based on the results obtained, we found that selenium photo-CVG at this acid concentration was efficient only if we applied a little heating on the solution entering the photochemical reactor. We obtained Se(IV) yields comparable to those of the classic CVG methods, while Se(VI) resulted much less efficient, with at least 10 times lower sensitivity respect to Se(IV), but, unlike hydride generation, still detectable at trace level. Method limit of detection (LoD) was 65 ng L<sup>-1</sup> (corresponding to an absolute LoD 8.5 pg) under the optimum experimental conditions and repeatability at 1 µg L<sup>-1</sup> Se(IV) was 0.6 % RSD (n = 5).

This analytical method was tested with several inorganic coexisting ions commonly present in real samples. We found nitrate ion enhanced selenium vapor photo-generation only in a very limited concentration range, with experimental trend much more similar to that of iodine than that of bromine. Cu(II) resulted the most interfering metal cation among those used in this work.

Finally, our method was validated by the analysis of the certified reference sample of natural water (NIST 1640a). The value found for Se(IV) analysis ( $19.73 \pm 1.10 \mu\text{g L}^{-1}$ ; n = 3) were in good agreement with the certified value ( $20.13 \pm 0.17 \mu\text{g L}^{-1}$ ), with a quantitative recovery from spiked blank (2 % HNO<sub>3</sub>). Ionic chromatography was, also, employed in order to evaluate possible analyte loss and/or conversion during the sample pre-treatment, proving to be an useful technique for inorganic selenium speciation.

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## Investigation of industrial polyurethane foams modified by electrosynthesized copper nanoparticles

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Since decades, polyurethane (PU) foams are being used in many fields as paddings, air and water filters, flame retarder, stiffening agents, and so on. The modification of polymeric materials with nanoparticles (NPs), to improve their physical, mechanical, and chemical properties has risen a great interest, as well<sup>1</sup>. When antimicrobial NPs (like Cu ones<sup>2</sup>) are used, the final composite material may retain antibacterial properties. When embedded in a polymer matrix, CuNPs can act as bioactive ion reservoirs, capable of exerting their ionic release activity over long time ranges. The kinetics and extent of the ion release from this class of composites have been already demonstrated to provide an efficient way to predict the final bioactivity of the (nano)material<sup>3</sup>.

In this work, we used colloidal CuNPs to modify industrial polyurethane foams by impregnation. CuNPs were electrochemically prepared under typical sacrificial anode electrolytic conditions<sup>4</sup>. The ion release properties were then quantitatively assessed by Electrothermal Atomic Absorption Spectroscopy operated on aliquots of physiologic contact solution (saline phosphate buffer) let in contact with the bioactive Cu/PU materials and then sampled at defined times.

We studied the possibility to tune Cu ion release by changing the nanoparticle loading in the composite and also by changing the particle composition. The latter was accomplished by properly selecting different NP capping agents during the electrochemical synthesis. In particular, two symmetric quaternary ammonium salts with different chain length were employed (i.e. tetraoctylammonium chloride and tetrabutylammonium chloride) and the ion release kinetics showed to be dependent of the alkyl chain length.

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## Evaluation of the growth orientation of molecules in PoAP thin films:

- *In situ* electrochemical growth by AFM
- Ar cluster ion etch profiles

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The electrochemical oxidation of ortho-aminophenol (oAP) on platinum substrates produces a polymer (PoAP) characterized by tuneable properties dependent on pH and, particularly, a strong passivating behaviour occurs in neutral media. Our previous studies [1-4] were focussed on the compositional and topographical characterization of the polymer itself, its inner and external interface, but, because it is very thin, the evaluation of the growth orientation of its molecules has required the additional use of advanced techniques for surface analysis, such as in situ Atomic Force Microscopy (AFM) and monochromatic X-ray Photoelectron Spectroscopy (XPS) depth profiling.

The in-situ investigation by Electrochemical-AFM allowed us to scan almost the same spatial region on the electrode, permitting space-time dependent images to be obtained. It revealed that on platinum substrates, already from the first cycle of PoAP electrosynthesis, there is a deposit of about 7-10 nm tall that does not increase in height during the following voltammetric scan cycles. These new results add valuable information, suggesting that the short PoAP chains, suspended by water molecules, are vertically aligned and progressively fill all platinum sites till an homogenous compact layer is formed on the electrode.

XPS depth profiles were obtained using a monochromatic X-ray source to better resolve close spaced chemical states. When a standard Ar<sup>+</sup> ion beam was used on our thin PoAP film, the chemical composition was significantly altered at the earliest stage of etching and a depth-profile analysis did not give reliable information. However, the Monatomic And Gas Cluster Ion Source (MAGCIS) from Thermo Scientific can be used to address this problem. The gentle, shallow sputtering from argon cluster ions does not cause subsurface damage, so the XPS data preserve chemical state information through the entire profile. MAGCIS was employed to achieve the main aim of this investigation; i.e. to observe the vertical distribution of polymer molecules in the film in order to clarify its mechanism of growth and add new information on the alignment of polymer chains. Particularly, it could be noted that the insulating PoAP is firmly attached to the platinum electrode by a unit that has monomer-like atom ratio. Additionally, this experiment could be an useful example of the efficiency of etching with the argon gas cluster-ion source.



The obtained results confirmed our previous assumptions on the mechanism of growth and have proved indications for the suitable use of poly(o-aminophenol) film as starting substrate for the development of biosensor devices and as Pt-coating membrane, opening interesting prospects for future works.

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## **Electrochemically produced ZnO nanoparticles: synthesis in aqueous medium and morphological/spectroscopic characterization**

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Nanostructured ZnO materials are receiving broad attention due to their distinguished performance in electronics, optics and photonics. Moreover, from the 1960s, they are widely used as effective antimicrobial agents, both in cosmetic and medical preparations<sup>1</sup>. Synthesis of ZnO nanostructures has been an active field in the last decade<sup>2</sup>. Besides classical chemical and hydrothermal methods, along with straightforward sol-gel procedures, electrochemical synthesis of ZnO nanoparticles (ZnONPs) is gaining increasing interest from the scientific community, being an easy, fast and green procedure. In fact, electrochemical processes in organic solvents (i.e. acetonitrile, alcohols, etc.) are flanked by novel synthetic strategies which use aqueous electrolytic media<sup>2</sup>. Based on our experience on the electrochemical synthesis of ZnO nanocolloids, prepared using anionic sodium polystyrene sulphonate (PSS) as stabilizer<sup>3</sup>, here we propose a novel approach with a cationic surfactant as NP capping agent, in basic NaHCO<sub>3</sub> solution. ZnONPs were prepared applying low current densities (10 mA/cm<sup>2</sup>) to twin pure zinc sheets. Two different reaction temperatures were studied (room temperature and 80°C), in the attempt to encourage the formation of stoichiometric oxides. The as-prepared colloidal mixtures underwent thermal treatments, in order to improve NP stability, morphology and stoichiometry. Different calcination temperatures were studied. Cetyltrimethylammonium bromide (CTAB) was used as stabilizer in the electrolytic aqueous medium. A systematic analytical characterization by transmission electron microscopy (TEM), UV-Vis, infrared (IR), and X-ray photoelectron (XPS) spectroscopies was performed to investigate the physicochemical properties of CTAB-capped ZnONPs at each stage of their production. Detailed curve fitting procedures were applied to XP signals, in order to assess Zn chemical speciation. For this purpose, both Zn photoelectronic and Auger emissions were taken into account. After calcination, morphological analyses revealed the presence of hexagonal, spherical and rod-like structures, for samples synthesized at room temperature. More ordered, variously branched, rod-like and rice-grain structures were obtained from the dispersions synthesized at 80°C. The most appealing nanostructures were obtained for the 300°C-calcined NPs prepared at 80°C, where regular rod-like NPs were observed. Based on these results, recently we developed a novel experimental set-up for electrochemical large-scale synthesis of ZnONPs. The novel apparatus allows producing grams of ZnONPs in short reaction times and with synthesis yields above 88%. These results are particularly appealing for perspective industrial applications of ZnO-based nanostructures<sup>3-4</sup>.

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## **A micro-invasive approach for the characterization of finishes on ancient monuments of Lecce (Puglia, Italy)**

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The use of organic materials in artworks is well known: substances like oils, proteins or waxes have traditionally been used as binders in different painting techniques or as natural waterproofing agents, for aesthetic, protective, hygienic and conservative purposes. For example since antiquity, natural hydrophobic materials were also employed in Lecce (Puglia, Southern Italy) on historical buildings, for the conservation of stone surfaces and the protection of facades decay. Between the 17th and 19th centuries, walnut oil, milk (caprine, ovine or bovine), leaf of the *Opuntia ficus-indica*, beeswax, and bulb of the *Drimia maritima* plant were employed on local stones (*carparo* and *pietra leccese*) as finishing.

Absence of written sources, aging and degradation reactions of applied substances with inorganic materials (intentionally added or derived from the stone support or environmental pollutants) make the correct identification of finish techniques an hard task.

Evidence of their presence are still visible on the facades of monuments of Lecce: a plurality of coloured finishes is observed, indeed, on the historical surfaces, mainly yellowish, pinkish, orange, who seem in some cases patinas coming from man-made stone treatments that possibly prevented the fast decay often observed on the calcarenites. Therefore, the correct characterization of the materials and methods used in the past by the local artists, who guarded them jealously, is of great important to conservation problems.

Several analytical procedures have been reported in literature for the analysis of art materials and, specifically, for the study of historical buildings: for example optical microscopy was used to study morphological variations of the stone substrate (treated or untreated), such as blackening and yellowing; contact angle and colorimetric measurements have been used to study the aesthetic and water repellent proprieties of lithotype and hydrophobic coating or monitor the state of conservation of monuments; FT-IR analysis has been used to acquire a deeper knowledge of the organic treatments and the interaction stone/treatment/environmental or for the chemical characterization of materials.

This research reports the study of some ancient recipes widespread in the past in the Salento (Puglia, Italy) on baroque buildings; according them, test specimens of *pietra leccese* and *carparo* were prepared and subjected to natural and accelerate aging. For an exhaustive characterization of ancient finishing techniques, different and complementary techniques were used, including optical (OM), dynamic contact angle and colorimetric measurements, and Fourier transform infrared spectroscopy (ATR-FTIR). Particular attention is given to the spectroscopic and colorimetric measurements, that are considered as an important non-

invasive analytical techniques to perform fast acquisitions, verifying the possible chemical and chromatic changes for different typologies of materials.

The main goal of this study is to gain information on the chemical composition and proprieties of examined treatments, with the main purpose of creating a database useful for the identification of ancient finishing techniques in the analysis of real samples taken from the surfaces of historic monuments.

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## **Titania based innovative nanocomposites to prevent stone artworks biodeterioration**

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Aesthetical and/or structural deterioration of stone substrates and artworks requires a series of actions able to retrieve or prevent and protect the work identity. The prevalently outdoor location of the majority of this type of artefacts involves a continuous maintenance, mainly consisting of periodical cleaning treatments. Today is very common the use of methods based on mechanical, physical and chemical systems directly acting on the causes of the stone degradation. In particular, chemical approaches involve the application via spraying, brushing, wraps or injection, of chemical products having both high efficacy and low toxicity to humans; moreover they are selected to not interfere with the materials constituting the artwork and to not be polluting. In this field one of the issue is the development of innovative materials that can add self-cleaning properties under UV-vis irradiation to the hydrophobic and consolidating properties of state-of-the-art commercial products.

In this paper we focused the attention on the modification of hydrophobic / consolidating polymers commonly used in the preservation of cultural heritage, such ESTEL 1100 and SILO 112, with low dispersions of titanium oxide nanoparticles. The idea was to incorporate a well-known material capable of adding photocatalytic properties, along with possible antimicrobial ones. Composite samples were prepared in the form of thin films, and were analyzed with proper analytical techniques. Specifically, x-ray photoelectron spectroscopy (XPS) was used to assess the surface chemistry; titanium ion release was studied by means of inductively coupled plasma mass spectrometry (ICP - MS). Moreover, the evaluation of titanium photocatalytic effect when embedded in the polymer matrices was investigated through UV - vis spectroscopy measurements. Finally, the composites were applied on some stone specimens and the chromatic variations were measured over the time.

Despite the absence of the titanium on the composites surface, the degradation experiments using UV irradiation show a good photocatalytic activity since almost total abatement of organic matter over a period of 72 hours is registered. This degradation was also proved to be faster with respect to materials without titanium nanoparticles.

## Characterisation of bioactive nanocomposites for stone conservation with VAR-FTIR spectroscopy

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Biodeterioration is one of the main decay processes of stone monuments because environmental parameters cannot be controlled. Conservation strategies are usually based on the application of biocidal products for biofilm removal and of protective water repellent coatings to control the bioreceptivity of the stone substrate. Biocides and water repellent materials may, however, negatively interfere and the biocide materials (quaternary ammonium salts) generally show short-term efficacy. Recently, combined materials including biocides and consolidants/water repellents have been proposed [1-5] and promising results have been obtained [6]. In particular, the research of the authors is focused on the development of nanocomposite materials with consolidant/protective properties and marked biocidal activity which is obtained by the progressive release of biocidal metal ions. Different nanocomposites have been proposed by embedding copper nanoparticles (Cu-NPs) [1], zinc oxide nanoparticles (ZnO-NPs) [2,3] or titanium oxide nanoparticles (TiO<sub>2</sub>-NPs) in commercially available silicon-based products.

In this work the authors present the results of the analysis of bioactive nanocomposite materials with variable angle reflectance (VAR) Fourier transform infrared (FTIR) spectroscopy. The nanocomposites are based on ZnO-NPs or TiO<sub>2</sub>-NPs embedded in Silo111 (water repellent) or Estel1100 (consolidant/water repellent). The aim of this study is to characterize the nanocomposites, follow the curing processes with time and to get insight into the possible interactions of the nanoparticles with the silicon based matrix materials.

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