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Programma Scientifico

Divisione di Chimica dell'Ambiente e dei Beni Culturali

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Keynote e Conferenze su Invito

- ABC/ANA/FIS KN01: Rocco Mazzeo, Department of chemistry, University of Bologna/Microscopy and Microchemistry Art Diagnostic Laboratory (M2ADL), Ravenna, Italy
- ABC/ANA/FIS KN02: Erika Ribechini, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13, 56124 Pisa, Italy
- ABC KN01: Raffaele Cucciniello, Dipartimento di Chimica e Biologia, Università di Salerno, Via Giovanni Paolo II,132 84084 Fisciano (SA), Italy
- ABC/ANA KN01: Antonio Marcomini, University Ca' Foscari of Venice, Italy
- ABC/ANA KN02: Davide Vione, Department of Chemistry, University of Torino, Via P. Giuria 5, 10125 Torino, Italy
- ABC/ANA KN03: Alessandra Genga, Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Lecce, 73100, Italy.

Macro Mid-Infrared total reflection (MA-FTIR) mapping for the characterization of outdoor bronze surfaces

Rocco Mazzeo[a], *Stjin Legrand*[b], *Giorgia Sciutto*[a], *Silvia Prati*[a], *Emilio Catelli*[a], *Paolo Oliveri*[c], *Koen Janssens*[b]

[a] *Department of chemistry, University of Bologna/Microscopy and Microchemistry Art Diagnostic Laboratory (M2ADL), Ravenna, Italy;* [b]*Department of chemistry, University of Antwerp, Antwerp, Belgium;* [c]*Department of Pharmacy-DIFARUniversity of Genoa, Genoa, Italy; rocco.mazzeo@unibo.it*

In the last decades, many research efforts have been devoted to the development of advanced non-invasive approaches for the examination of cultural heritage. However, up to now, too few attentions has been paid on the potentialities of the Macro Mid-Infrared total reflection (MA-FTIR) mapping analysis. Indeed, the infrared reflectance spectroscopy single point investigation has been largely applied in analytical studies of artworks due to its advantage of characterizing both organic and inorganic materials. On the other hand, the possibility to simultaneously obtained information on molecular composition and spatial distribution of constituents is of crucial importance for properly addressing conservation issues.

To this aim, the present research work was focused on the application of an advanced MA-FTIR mapping system for the study of altered bronze surfaces. Moreover, an *ad hoc* multivariate approach has been proposed for the interpretation of data.

A bronze sculpture exposed in the atmosphere deteriorates with time, developing a greenish/blackish layer mainly constituted of corrosion products. The formation of these corrosion products implies complex chemical, electrochemical and physical processes that strongly depend on the constituents of the surrounding environment. In addition, different acrylic resins, synthetic waxes and organic inhibitors may be commonly applied for short-term protection of outdoor bronze sculptures.

To the Authors knowledge for the first time Mid FTIR macro mapping analysis was performed on metal patinas, allowing the location of corrosion products and old coatings, and describing their interactions. The performances of the approach have been initially evaluated on standard bronze samples characterized by the presence of a green basic hydroxysulfate (brochantite) treated with different organic materials. Subsequently, the exceptional case of study of the bronze sculptures of the Neptune Fountain (Bologna, 16th century) has been investigated.

The instrument acquired hyperspectral cubes by scanning the metal surface without any contact, recording sequential total reflection single-point spectra. The big dimension of the data cubes obtained, as well as, the deformation of IR bands induced by specular reflection phenomena, may serious hampering the correct interpretation of the spectral features. Thus, a chemometric method, based on the use of the brushing procedure, was proposed to extract all the useful information embedded in a complex hypercube.

The high specificity of MA-FTIR mapping revealed important outcomes on the state of conservation of the monumental statue. In particular, it was possible to clearly describe well preserved areas in which wax and incralac resulted to be still present, describing their distribution and identifying zones affected by a more aggressive corrosion process.

GC/MS and HPLC/MS characterization of organic residues from ceramic vessels of Basque whalers of the 16th to 17th century

Erika Ribechini[a], *Laura Blanco-Zubiaguirre*[b], *Ilaria Degano*[a], *Jacopo La Nasa*[a], *Javier García-Iñañez*[c], *Maitane Olivares*[b], *Kepa Castro*[b]

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The aim of this work is focused on the identification of the organic residues from ceramic vessels recovered from a deposit in Lekeitio (Basque Country, Northern Spain). These vessels are suspected to have been used by the Basque whalers in the period from 16th to 17th Century to store whale oil. Bearing in mind our aim, different analytical approaches based on chromatography and mass spectrometry (GC/MS and HPLC-ESI-qTOF) were used to study both fresh blubber and whale oil products and the archaeological substances in order to obtain chromatographic profiles and possibly detect highly diagnostic biomarkers. Two hydrolysis approaches were used in order to compare data and obtain as much information as possible; (i) microwave assisted direct hydrolysis of the ceramic samples and (ii) microwave assisted hydrolysis of previously solvent-extracted samples. On the other side, the study of solvent (chloroform:hexane (3:2 v/v)) soluble fraction was carried out by means of HPLC-ESI-qTOF. Preliminary results led to the identification of some interesting organic compounds in the hydrolysable and soluble aliquots from the ceramic vessel such as pristane, phytane, several saturated fatty acids, hydroxyacids and cholesterol along with triacylglycerols in the solvent soluble fraction. On the other hand, the obtained results for the fresh whale oil and blubber suggested a similar lipid profile to the ones obtained for the archaeological samples. The chemical results together with archaeological data seem to indicate the vessels were used to store whale oil.

A new passive sampler for atmospheric NO_x determination

Raffaele Cucciniello[a], *Rosa La Femina*[a], *Ilaria Zarrella*[b], *Concetta Pironti*[a], *Oriana Motta*[b], *Antonio Proto*[a]

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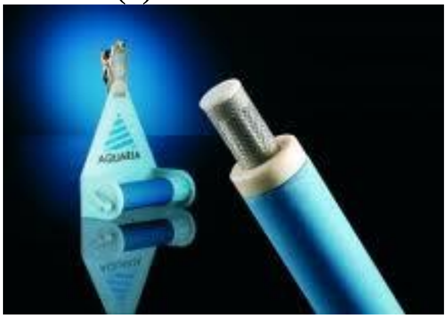
Atmospheric nitrogen oxides, NO and NO_2 (NO_x), are important polluting compounds, representative of gaseous emissions. NO_x concentrations are often used as a tracer of traffic related air pollution (1,2) and have been associated with adverse health effects and mortality in epidemiological studies.
Conventional NO_x measurements are typically conducted by using a chemiluminescence analyzers. Notwithstanding, a cost-effective alternative and simpler measurement technique for assessing air quality may be the use of passive devices (3).



De Santis and coworkers, to the best of our knowledge, have developed a passive sampler for NO_x (NO + NO_2) in the air by using an axial device and TEA/CrO_3 as reactive sorbent (4).
In this context, we were interested to search an alternative and environmentally friendly methods that could, on the one hand, collect NO and NO_2 simultaneously and, on the other, allow to overcome the environmental concerns related to the use of CrO_3 as substrate. In this paper, we report on the use of Na_2CO_3-impregnated silica as reactive substrate for atmospheric NO_x using a new passive sampler device.
The present study pursues three specific objectives:
- to explore new substrates for the simultaneous measure of NO to NO_2 overcoming environmental concerns connected to the use and disposal of CrO_3 as oxidant agent.
- to perform calculation of the diffusion sampling rate of the passive samplers.
- to perform validation experiments in the laboratory and in the outdoor environment, by the correlation of NO and NO_2 measured by passive samplers and with co-located chemiluminescence analyzer.

References
1. E. A. Riley et al. *Atmos. Environ*. (2016) 132, 229-239; **2.** B. Beckerman et al. *Atmos. Environ.* (2008) 42, 275-290; **3.** J. N. Cape *Critical Rev. Anal. Chem.* (2009) 39, 289-310; **4.** F. De Santis et al. *Anal. Bioanal. Chem.* (2002) 373, 901-907.

An integrated modelling approach to study the impacts of nutrients on coastal aquatic ecosystems in the context of climate change

Marco Pesce [a], Andrea Critto[a,b], Silvia Torresan[a,b], Monia Santini[b], Elisa Giubilato[a], Lisa Pizzol[a], Paola Mercogliano[b], Alberto Zirino[c], Ouyang Wei[d], Antonio Marcomini[a,b]

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Increase of atmospheric greenhouse gases (GHGs) due to anthropogenic activities is causing changes in Earth's climate. Global mean temperatures are expected to rise by 0.3 to 4.8 °C by the end of the 21st century, and the water cycle to be affected by changes in global atmospheric moisture. Coastal waterbodies such as estuaries, bays and lagoons, together with the ecological and socio-economic services they provide, could be most affected by the ongoing changes on climate being subjected to the combined changes in the physico-chemical processes of atmosphere, upstream land and coastal waters. Particularly, climate change is expected to alter phytoplankton communities by changing climate and environmental drivers such as temperature, precipitation, nutrient loadings and concentrations, and to exacerbate the symptoms of eutrophication events such as hypoxia, harmful algal blooms and loss of habitat. A better understanding of the links between environmental drivers and phytoplankton communities is necessary for predicting climate change impacts on aquatic ecosystems. In this context, the integration of climate scenarios and environmental models is a valuable tool for the investigation and prediction of phytoplankton ecosystem dynamics under climate change conditions. In the last decade, the impact of climate change on the environmental distribution and cycling of nutrients, including effects on aquatic ecosystems, prompted modeling studies at a catchment scale, mainly related to lake ecosystems. The further development of integrated modeling approaches to other types of waterbodies such as coastal waters can be a useful contribution to increase the availability of management tools for ecological conservation and adaptation policies. Here we present the case study of the Zero river basin (ZRB) in Italy, one of the main contributors of freshwater and nutrients loadings to the salt-marsh Palude di Cona (PDC), a waterbody belonging to the lagoon of Venice. To predict the impacts of climate change on nitrogen (N) and phosphorus (P) loadings of the ZRB and the consequent effects on the coastal phytoplankton community of PDC, we applied an approach integrating an ensemble of GCM-RCM climate projections, the hydrological model SWAT and the ecological model AQUATOX. Climate scenarios for the area indicated an increase of precipitations in the winter period and a decrease in the summer months, while temperatures show a significant increase over the year. The hydrological model SWAT predicted changes in water discharge and nutrient loadings of the ZRB, pointing out an increase in the winter period and a reduction during the summer months for both parameters. Simulations with AQUATOX predicted changes in water temperature, nutrient concentrations and N:P ratios, and consequent variations in the biomass and composition of phytoplankton in PDC, with major changes observed in the spring-summer period, where the abundance of warm-adapted species increases noticeably (1).

References

1. Pesce et al., 2017.

Photoinduced Processes in Surface Waters: A Photochemical Mapping of Sweden

Davide Vione[a], *Birgit Koehler*[b], *Francesco Barsotti*[a], *Marco Minella*[a], *Claudio Minero*[a], *Lars J. Tranvik*[b], *Tomas Landelius*[c]

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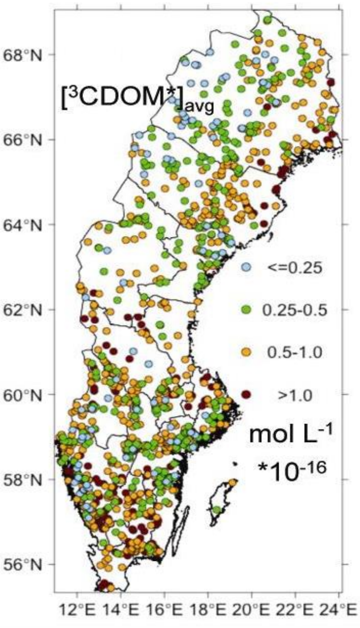
Photochemical reactions induce the self-depuration of surface waters, particularly against polar biorefractory pollutants that include many emerging contaminants (1). Photoreactions are divided into direct photolysis and indirect photochemistry. Direct photolysis involves sunlight-absorbing pollutants, and transformation is triggered by photon absorption. Indirect photochemistry takes place when sunlight is absorbed by naturally occurring compounds called photosensitisers (e.g., nitrate, nitrite and chromophoric dissolved organic matter, CDOM) to produce reactive transient species such as the hydroxyl ($^{\bullet}$OH) and carbonate ($CO_3^{\bullet-}$) radicals, singlet oxygen ($^1O_2$), and CDOM triplet states (^{3}CDOM*) (2,3).

We have recently modeled photochemical processes in surface waters (4), predicting the phototransformation kinetics of pollutants and deriving photochemical parameters from available time series of water chemistry. In the latter case, one can get insight into the impact of climate change over photochemistry (5). Here we show the application of photochemical modeling to data from a large geographic region. Based on a wide dataset that includes over 1000 Swedish lakes with their average depth, water chemistry and the incident sunlight irradiance, we could predict the steady-state [$^{\bullet}$OH], [$CO_3^{\bullet-}$], [$^1O_2$] and [^{3}CDOM*]. This is the first ever photochemical mapping of a country's inland waters.

The model results were validated by comparison of available field data with the predicted photochemical lifetimes of carbamazepine and ibuprofen in Lake Boren (6). Based on the photochemical map, and compared to temperate lakes, the CDOM-rich boreal lakes of Sweden are dominated by ^{3}CDOM* processes (except for the lakes located in the NW part of the country). In contrast, the efficient scavenging of $^{\bullet}$OH and $CO_3^{\bullet-}$ limits the importance of the relevant reactions. The ^{3}CDOM* processes are particularly effective towards the degradation of phenols, phenylurea herbicides and sulfonamide antibiotics (7). CDOM is a key photosensitiser in most Swedish lakes and strongly prevails over nitrate and nitrite. Climate change is expected to produce water browning in boreal lakes including the Swedish ones, due to export of light-absorbing organic compounds from soil to surface waters (8). Browning enhances the levels of CDOM, which is the ^{3}CDOM* precursor. Therefore, the importance of the ^{3}CDOM*-induced processes is expected to increase even more in the future, in Swedish lakes as well as in many other boreal areas.



Modelled steady-state [^{3}CDOM] in the 1048 Swedish lakes under study*

References

1. *Analytical Chemistry* 2011, *83*, 4614−4648; **2.** *Chemistry - A European Journal* 2014, *20*, 10590−10606; **3.** *Chemical Reviews* 2015, *115*, 13051−13092; **4.** *Environmental Science: Processes and Impacts* 2014, *16*, 732−740; **5.** *Science of the Total Environment* 2016, *541*, 247-256; **6.** *Environmental Science & Technology* 2015, *49*, 1646−1653; **7.** *Chimia - International Journal for Chemistry* 2007, *61*, 641−644. 8. *Global Change Biology* 2011, *17*, 1186−1192.

Primary and secondary carbonaceous species in PM10 and PM2.5 samples

Alessandra Genga[a], *Maria Siciliano*[a], *Cosimino Malitesta*[a], *Tiziana Siciliano*[b], *Antonio Proto*[c], *Raffaele Cucciniello*[c]

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Carbonaceous PM is composed of a refractory component, commonly called elemental carbon (EC), and an organic fraction, called organic carbon (OC). Organic aerosols represent a large fraction of atmospheric aerosols. The organic fraction can include saturated and unsaturated aliphatic compounds, aromatic compounds, alcohols, ketones, aldehydes, carboxylic acids, amines, sugars, polyols, and organic sulfur compounds (2). Organic and elemental carbon were measured in daily PM10 and PM2.5 and 6 hours range time PM2.5 samples collected from September 2015 to October 2015 in a coastal rural site near Brindisi in the Apulia region (Italy), in order to determine factors affecting the carbonaceous aerosol variations. OC and EC were measured on Sunset Laboratory Thermal–Optical Carbon Aerosol analyser using NIOSH protocol.

Carbon content (total carbon TC) represented a considerable fraction for both PM10 and PM2.5. The highest values for both parameters were recorded when the winds blows from NE Europe and when Sharan Dust events have been recognized. The results show that OC and EC exhibited higher concentrations during the night hours, suggesting that stable atmosphere and lower mixing play important roles for the accumulation of air pollutants and hasten condensation or adsorption of volatile organic compounds.

Moreover, ATR-FTIR analysis were performed on some samples with the lowest and the highest OCsec and on samples characterized by Saharan Dust event. FTIR spectroscopy provides absorption peaks which can be identified and assigned to chemical bonds to identify functional groups in a complex sistem. The FTIR method is relatively simple and rapid and requires only small sample size. To our knowledge, there are only few examples of recent studies which are subjected to quantification or qualification of chemical species of aerosol samples. FTIR coupled with attenuated total reflectance (ATR) is a new technique developed recently. ATR FTIR analysis were carried out and it let identify organic functional groups included non-acid organic hydroxyl C-OH group (including sugars, anhydrosugars, and polyols, herein indicated as alcohol group), aromatic C=C-H group, aliphatic unsaturated C=C-H group, aliphatic saturated C-C-H group, non-acid carbonyl C=O group, carboxylic acid COOH group, and amine NH2 group. Among the inorganic ions, carbonates, sulfate, silicate and ammonium can be recognized.

References:
1. Genga A., Ielpo P., Siciliano M., Siciliano T., Carbonaceous particles and aerosol mass closure in PM2.5 collected in a port city 2017. Atmospheric Research 183, 245-254
2. Gilardoni, S., Liu, S., Takahama, S., M. Russell, L., Allan, J.D., Steinbrecher, R., Jimenez, J. L., De Carlo, P.F., Dunlea, E.J., Baumgardner D., 2009. Characterization of organic ambient aerosol during MIRAGE 2006 on three platforms. Atmos. Chem. Phys., 9, 5417–5432

Comunicazioni Orali

Formulation and characterization of hydroxypropyl guar based gel-like systems, tailored for the low impact cleaning of works of art surfaces

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The development and characterization of a new family of water based gel-like systems containing hydroxypropyl guar gum (HPG) with borax as crosslinker are presented in this contribution. In the formulation glycerol is introduced as plasticizer, and its role is broadly investigated. The effect of the components on the structure, on the viscoelastic behavior of the system and on the activation energy related to the relaxation process has been investigated by means of rheology, Nuclear Magnetic Resonance (NMR) and Small Angle X-ray Scattering (SAXS) (1,2). Results indicated that the mechanical properties of the systems can be tuned by varying the amount of each component; ^{11}B-NMR and ^{1}H-NMR measurements highlighted the role of glycerol in the crosslinking mechanism, with the formation of a glycerol-borate complex. The characterization approach is used to identify the best formulation, in the view of a future application in the field of cultural heritage conservation, in particular for the cleaning of surfaces of historical and artistic interest (3). The main goal is to obtain a system adaptable to the roughness typical of surfaces of many artifacts. The best formulation was used for preliminary cleaning tests on a *stucco* artifact deriving from the decorations of *La Fenice* theatre, in Venice. The tests suggest a promising efficacy in selective cleaning of the surface and make these materials particularly interesting in the field of restoration.

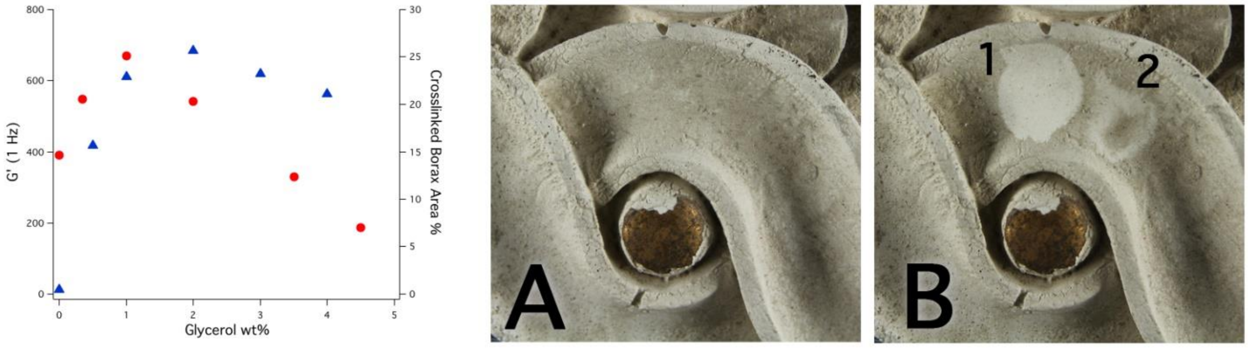

Figure 1: On the left, Storage modulus values at Frequency=1Hz (■) and Crosslinked Borate Area obtained from NMR measurements (▲) are plotted against glycerol concentration. Pictures on the right show the *stucco* surface before (A) and after (B) the cleaning, with the comparison between the the HPG based system (1) and a wet cotton swab (2).

References
1. T. Coviello, P. Matricardi, F. Alhaique, R. Farra, G. Tesei, S. Fiorentino, F. Asaro, *e-XPRESS Polym. Lett.* 2013, **7**, 733. 2. Y. Cheng, K.M. Brown, R.K. Prud'homme, *Biomacromolecules*, 2002, **3**, 456. 3. I. Natali, E. Carretti, L. Angelova, P. Baglioni, R.G. Weiss, L. Dei, *Langmuir*, 2011, **27**, 13226.

Chemical poly ethyl methacrylate (PEMA) organogels for the removal of pressure sensitive tapes (PSTs) from paper artworks

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Chemical poly ethyl methacrylate (PEMA) organogels loaded with Diethyl Carbonate (DEC) were synthesized by means of radical polymerization (1, 2). These systems are specifically designed for the removal of degraded Pressure Sensitive Tapes (PSTs) from paper artworks, a very common issue in the field of manuscripts and drawings restoration. DEC, an organic green solvent, shows interesting swelling properties towards PSTs components; besides it is inert to most common inks and dyes, unlike other commonly used cleaning systems such as polar solvents and microemulsions (3).

Several organogels were obtained by changing reaction parameters; on the basis of macroscopic evaluations (e.g. mechanical properties, homogeneity), some systems were chosen for a deep physico-chemical characterization performed by means of different techniques. Thermogravimetry (DTG), Differential Scanning Calorimetry (DSC), and gravimetric analysis were used to assess solvent content and uptake/release behaviour of gels; rheological analysis permitted the evaluation of their viscoelastic properties; Fourier Transform Infrared Spectroscopy (FT-IR) and Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) allowed to investigate the presence of unwanted residues in the exchange solvents and the effectiveness in the removal of PSTs. The penetration of DEC through the backing layer of PSTs and the swelling of the adhesive was investigated by means of Laser Scanning Confocal Microscopy (LSCM).

Cleaning tests on mock-up samples and real artworks were also successfully performed.

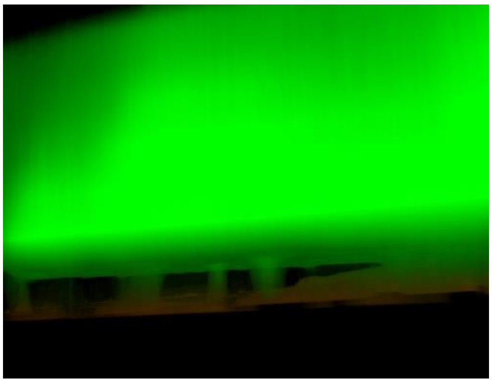

Fig. 1 – Laser Confocal image of a PEMA-DEC gel onto a PST sample: penetration of DEC (in green) through the backing up to the adhesive layer (in red)

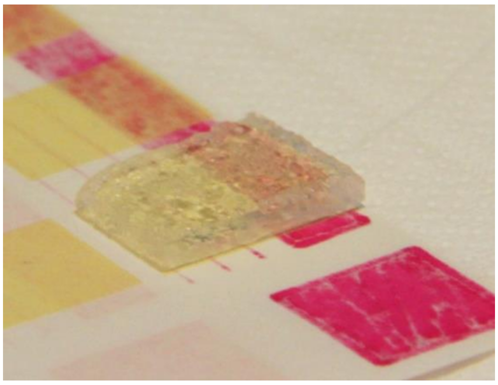

Fig. 2 – Application of a PEMA-DEC organogel for the removal of a Masking Tape from a mock-up sample

References

1. M. D. Pianorsi, M. Raudino, N. Bonelli, D. Chelazzi, R. Giorgi, E. Fratini, P. Baglioni, Pure Appl. Chem., 2017. 2. K. K. Chee, Polymer Gels and Networks 5, 95-104, 1997. 3. F. Mizia, M. Notari, F. Rivetti, U. Romano, C. Zecchini, Chimica & Industria - Aprile 2001.

Surface Cleaning of Artworks: Structure and Dynamics of Nanostructured Fluids Confined in a Polymeric Network

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Nanosystems and confinement tools for the controlled release of a cleaning agent, e.g., hydrogels and microemulsions, have been used for several years for the treatment of delicate surfaces in art restoration interventions. However, notwithstanding the unprecedented achievements from an applicative point of view, a fundamental comprehension of their interaction mechanism is still lacking. In this study PVA hydrogels, obtained via freeze-thaw processes, are prepared as scaffolds for water-based nanostructured fluids for application in the cleaning of artworks: rheological, thermal, microscopic and scattering techniques showed that, depending on the number of freeze-thaw cycles, the hydrogels exhibit different physicochemical and viscoelastic properties, making them suitable for application in a broad range of cleaning issues. The gels have been loaded with an oil-in-water microemulsion and the diffusion of the microemulsion droplets inside the polymeric network has been investigated through Fluorescence Correlation Spectroscopy (FCS), demonstrating that the microemulsion is permanently kept inside the matrix and can freely diffuse in the network. In addition, we show that, when the gel-microemulsion system is put in contact with a layer of hydrophobic grime, a dynamic interaction between the microemulsion droplets and the underlying layer is established, leading to the solubilization of the hydrophobic molecules inside the droplets in the gel matrix. Thus, for the first time, through FCS, insights about the removal mechanism of hydrophobic grime upon interaction with cleaning agent embedded in the polymeric matrix, are obtained. Some examples of significant case studies treated with these innovative materials will be presented.

Nanocomposites for the consolidation and deacidification of cellulose-based artifacts

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A restoration method designed for the conservation of degraded fibrous-based artifacts should addressed the two main problems concerning these materials. Firstly, a mechanical reinforcement of artifacts is usually needed to ensure that the original material keeps its integrity. Moreover, pH buffering is required to prevent acidic degradation that is inherent to natural materials. (1)

It has been recently shown that these two issues are related. For instance, it takes less than 100 years for acidic compounds to induce a significant loss of mechanical properties in canvases based on natural materials. (2) The same degradation effect of acidic compounds is found in paper-based artworks, drawings and documents. In this regard, several deacidification methods have been proposed and proven efficient in hampering the degradation of cellulose. (3,4,5)

Research efforts have been recently devoted to the development of a nanocomposite material for the consolidation and concomitant pH adjustment of cellulosic works of art and artifacts that is one of the goal within the EU Project NANORESTART.

The use of nanocellulose, in combination with nanoparticles and cellulose derivatives, could ensure the consolidation of fiber-based materials using almost entirely natural materials. The choice of these materials is due to the high compatibility of the proposed treatments with the original fibrous support, which is essential from the conservation point of view.

Considering the high variability of cellulose-based artifacts, several different approaches were followed in order to provide conservators with a wide palette of tools that can be used on different works of art that are in need of both consolidation and deacidification treatments.

Nanocomposite materials were analyzed in order to gain more information about their structure and characteristics. Mechanical tests on not aged and aged reference samples were used to assess the consolidation efficacy of the proposed consolidation treatments before testing on real case studies.

References

1. J. W. Baty, C. L. Maitland, W. Minter, M. A. Hubbe, and S. K. Jordan-Mowery, BioResources 5, 1955 (2010). 2. M. Oriola, A. Možir, P. Garside, G. Campo, A. Nualart-Torroja, I. Civil, M. Odlyha, M. Cassar, M. Strlic, Anal. Meth. 6, 86-96 (2014). 3. R. Giorgi, L. Dei, C. Schettino, and P. Baglioni, in Prepr. IIC Balt. Congr. 2002, Work. Art Pap. Books, Doc. Photogr. Tech. Conserv., edited by V. Daniels, A. Donnithorne, and P. Smith (International Institute for Conservation, Baltimore, 2002), pp. 69–73. 4. G. Poggi, R. Giorgi, N. Toccafondi, V. Katzur, and P. Baglioni, Langmuir 26, 19084 (2010). 5. G. Poggi, N. Toccafondi, L. N. Melita, J. C. Knowles, L. Bozec, R. Giorgi, and P. Baglioni, Appl. Phys. A 114, 685 (2014).

FIB-FESEM-EDX study of silver Roman coins: characterization of the core microstructure and corrosion products with a multi-analytical approach

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Metal artifacts are among the most common materials in the Cultural Heritage field: alloys have been used in several fields of everyday life and their analysis can prove useful information about the technology of the ancient populations. In particular, coins are important for studying provenance, dating, minting and corrosion processes as well as provenance and stratigraphy of the archaeological sites (1,2).

In this work a set of Roman silver coins, dated back to the Antonini's period, has been analyzed using FIB-FESEM-EDX aiming to establish the used technique for the silvering and discriminating different mints. Recently, this approach was used as a complementary technique for the characterization of bronze coins (3) but this is the first application on Roman silver coins. The aim of this work is to investigate the microstructure and the composition of the alloy with a micro-invasive approach. Commonly to investigate the composition of the metal core are used invasive and destructive techniques, therefore the developing of methods with minimal damage on metal is of a great interest.

The study of Antonini's coins is also important as in that historical period Roman Empire underwent to a severe debasement which influenced coinage, so the surface silvering it is still an open question. Diocletian in the 294 A.D. introduced a complex alloy (Cu-Sn-Pb-Ag) with an Ag-rich surface patina of 2 µm. Some coins of the set show a very fine silvered surface with a core composition entirely made of Cu, whereas others have the composition made of Sn-Cu-Pb with a very low concentration of Ag. This technique has been joined with surface analysis (Raman spectroscopy, SEM mapping, voltammetry of microparticles (VMP) and electrochemical impedance spectroscopy (EIS)) for a deeper knowledge of the samples. The results showed the leaching of the Sn and Pb as well as of the Cu that formed several common products on the surface of the coins, *i.e*, Cu_2O, CuO, PbO, SnO. The presence of AgCl has been detected in several coins.

In conclusion, FIB-FESEM-EDX analysis provides information about the composition, structure and thickness of the metal patina as well as the composition and microstructure of the metallic core which in turn reflects the technology of minting. As a result, FIB-FESEM-EDX features yield information for the diagnostic, authentication, technologies and historical context in which the coins were fabricated. Such multi-analytical data allow us the possibility of screening the coins minting, obtaining significant differences between those minted in Roma and those minted in the Gallia.

References

1. Domènech, A. et al., *Electroanalysis*, 23(12), pp.2803–2812 (2011). **2.** Di Turo, F. et al. *Analytica Chimica Acta*, 955, pp.36-47 (2017). **3.** Doménech-Carbó, A. et al., *Talanta*, 169, pp.50–56 (2017).

I materiali e la tecnica pittorica di Konrad Witz nel suo capolavoro di Ginevra

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Konrad Witz, tedesco di origine, ma attivo soprattutto in Svizzera fra il 1431 e il 1445 circa, è, per dirla con le parole dello storico dell'arte Jonathan Jones, "un gigante della pittura medievale che aspetta solo di essere scoperto". Le opere superstiti di questo artista sono davvero poche; fra queste sicuramente le più importanti sono le due tavole dipinte nel 1444 su entrambi i lati per l'altare maggiore della Cattedrale di Ginevra ed ora conservate nel Musée d'art et d'histoire de Genève (1). Il presente studio illustra i risultati della campagna diagnostica condotta, prima dell'intervento di restauro, sui materiali costitutivi, la tecnica esecutiva e lo stato di conservazione di queste opere. Le indagini scientifiche sono state condotte dapprima mediante tecniche strumentali non invasive, successivamente su microcampioni prelevati in modo mirato dopo l'acquisizione dei dati delle analisi preliminari.
Gli obiettivi delle indagini sono così sintetizzati:

- osservazione in situ della superficie delle opere mediante l'impiego di microscopia a bassi ingrandimenti, in luce visibile e UV, per osservare lo stato di conservazione della pellicola pittorica originale e differenziare le parti originali dalle eventuali ridipinture;
- analisi XRF in più punti delle superfici policrome per avere dati preliminari sulla composizione degli elementi chimici e orientare la scelta dei prelievi di campione;
- esame chimico-stratigrafico di campioni di materiale pittorico per documentare la composizione delle stratificazioni dei materiali costitutivi, dalla preparazione fino alle vernici superficiali, e avere così informazioni circa la tecnica esecutiva;
- identificazione delle cariche minerali negli strati preparatori e dei pigmenti nelle stesure pittoriche;
- riconoscimento, mediante test microchimici ed istochimici, delle classi di appartenenza dei leganti organici nelle varie stratificazioni;
- identificazione dei leganti pittorici mediante gascromatografia abbinata alla spettrometria di massa (GC-MS).

Una prima ricognizione delle superfici pittoriche delle quattro opere è stata effettuata mediante l'impiego di uno stereo-microscopio operativo con sorgenti di luce visibile e UV. Successivamente, sono state analizzate le superfici pittoriche mediante uno spettrofotometro portatile a raggi X (XRF). Sui dipinti sono state, inoltre, eseguite indagini radiografiche e riflettografiche all'IR per studiarne lo stato di conservazione e esaminare i dettagliati disegni preparatori. Una volta acquisite in situ tutte queste informazioni sono stati effettuati sedici microprelievi di materiale pittorico in zone ritenute maggiormente significative in relazione alle domande di conoscenza.
I test microanalitici impiegati sono stati finalizzati alla ricerca di sostanze proteiche, composti saponificabili e polisaccaridi. Le analisi rivolte all'identificazione dei leganti organici sono state condotte mediante microspettroscopia infrarossa a trasformate di Fourier e gascromatografia accoppiata alla spettrometria di massa (GC/MS).

References
1. C. Lapaire, A. Rinuy, *Le retable de la cathédrale de Genève*, in Zeitschrift für Schweizerische Archaologie und Kunstgescheichte, Band 44, 1987.

Towards the Non-invasive Proteomic Analysis of Cultural Heritage and Archaeological Objects

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During the last years, there has been a growing interest in the identification of proteinaceous material of cultural heritage and archaeological objects. Our group recently developed a new method for the non-invasive analysis of proteins material from precious and ancient artworks. The technique uses a functionalized film that extracts the proteins from the surface of the object. The extracted proteins are then analyzed by LC-MS/MS analysis using shotgun proteomics (1).

In this research, we will present the application of this method to several historical and archaeological samples. Moreover, we will discuss the analytical performances for the identification and quantification of proteins in complex matrixes.

In particular, we will present the developed protocol and the results obtained from the analysis of several artworks: a polychrome wooden altarpiece from the Maestro of Oropa, a polychrome sandstone capital, a rare polychrome alabaster, several wood medieval and renaissance panels (Pietro Gallo from Alba, Defendente Ferrari, Martino Spanzotti, Jean Bapteur, Gerolamo Giovenone) and a detached fresco from Antoine de Lonhy.

Moreover, through the use of this method we were able to identify the animal origin of an old precious manuscript from Domenico della Rovere (XIV century) as well as the binders from a rare sample of painted leather casket from Parisian manufactory (beginning of XIV century).

The analysis of the bottom of several greek vessels (Pyxis, Krater, Kylix cup and Kantharos) revealed the presence of animal origin proteins.

In conclusion, this study will report the first use of this non-invasive method for the characterization of proteins from ancient objects without the need to transport or sampling the artifacts.

References

1. M. Manfredi, E. Barberis, F. Gosetti, E. Conte, G. Gatti, C. Mattu, E. Robotti, G. Zilberstein, I. Koman, S. Zilberstein, E. Marengo, P. G. Righetti, Method for Noninvasive Analysis of Proteins and Small Molecules from Ancient Objects, Anal. Chem. 2017, 89, 3310–3317.

Provenance of Bitumen from different Apulian Bronze Age settlements through a biomarker based approach

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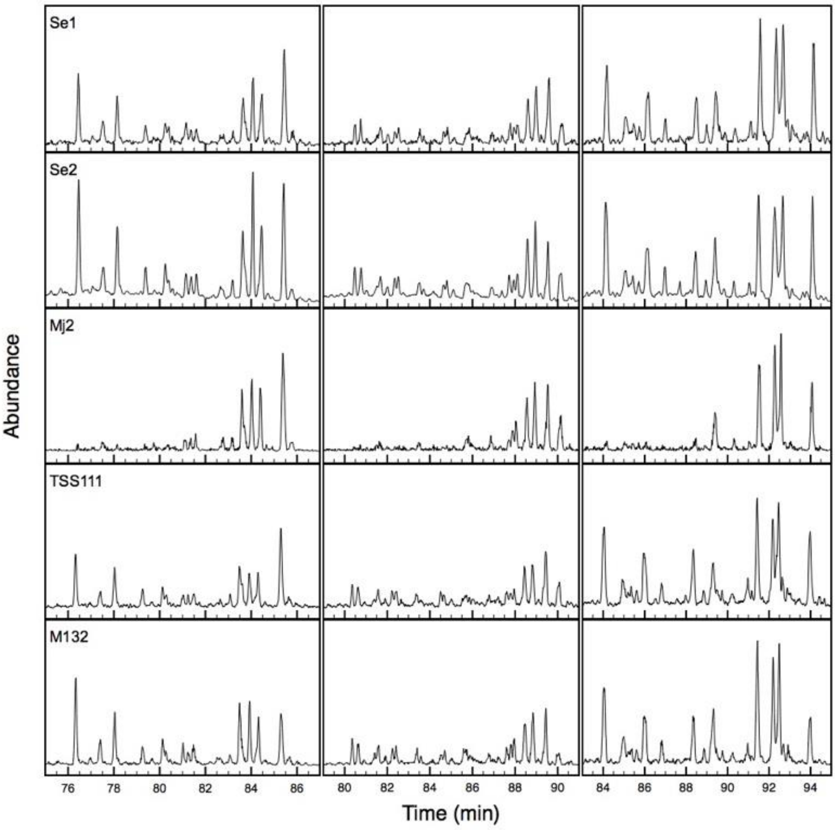
Bitumen has been used frequently in the Near East throughout history until modern times. Natural bitumen, found in solid or liquid form, was exploited and processed by ancient populations in Egypt, Mesopotamia and Syria for several uses such as to repair broken pottery, to waterproof containers or boats, to build the massive ziggurat temple mounds or to haft composite flint tools (1,2,3).
Together with the more widely studied and archaeologically important bitumen deposits in the Near East and Middle East (4,5), there are several seepages in Central Mediterranean which deserve more attention with respect to their exploitation and circulation in Antiquity. Evidence of bitumen use was found at several Apulian Bronze Age coastal sites (6), such as Otranto, Roca, Le Pazze (Lecce), Scoglio del Tonno (Taranto), Monopoli (Bari) and Torre Santa Sabina (Brindisi), but there are no archaeometric data about the relevant source(s).



Different bitumens from the central mediterranean sea region were studied as a possible source and analysed together with the archaeological samples using a geochemical, biomarker-based approach. The compositions of geological and archaeological samples were determined and provenance established. In the present communication, the relevant results will be described.

Acknowledgments

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References:
1. Connan, J., Nieuwenhuyse, O., Van As, A., Jacobs, L., 2004. Bitumen in early ceramic art: Bitumen-painted ceramics from Late Neolithic Tell Sabi Abyad (Syria). Archaeometry 46, 115-124. **2.** Connan, J., 2012. Le bitume dans l'Antiquité. Éd. Errance, collection Les Héspérides, Arles. **3.** Moorey, P.R.S., 1999. Ancient Mesopotamian materials and industries: The archaeological evidence. Eisenbrauns, Winona Lake, Indiana. **4.** Nissenbaum, A., Buckley, S., 2013. Dead sea asphalt in ancient Egyptian mummies—why? Archaeometry 55, 563-568. **5.** Connan, J., Van de Velde, T., 2010. An overview of bitumen trade in the Near East from the Neolithic (c.8000 BC) to the early Islamic period. Arabian Archaeology and Epigraphy 21, 1-19. **6.** Guglielmino, R., 2012. Il bitume di Roca. Breve nota su una sostanza negletta negli studi di protostoria italiana. Annali della Scuola Normale Superiore di Pisa 4/2, 99-114.

From XAES signals to depth-profile reconstruction: the case of copper and copper alloys

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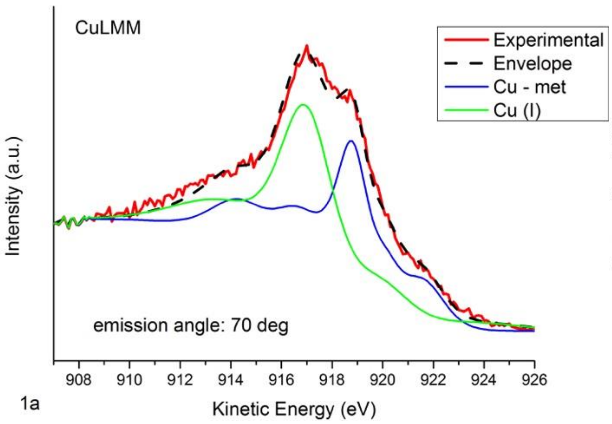
The analysis of the chemical state of co-existing copper and Cu (I) compounds by XPS is difficult since the Cu2p signal does not show any chemical shift. On the contrary the XAES signal $CuL_3M_{45}M_{45}$ allows distinguishing between Cu (0) and Cu (I) compounds. An analytical method starting from curve fitting of composed Auger induced CuLMM signals based on standards that permits quantifying the amount of copper and Cu_2O on the surface of brasses was developed and the thickness of the contamination and oxide nanolayers on the brass samples was determined by applying the three-layer model to standard XPS signals (1).

An alternative non-destructive way to reconstruct the in depth composition profile of a nano-layered surface by XPS involves the acquisition of angle resolved XPS spectra. An ARXPS experiment provides information on the intensities of the photoelectron signals vs emission angle: the higher is the emission angle, the more intense are the signals of the elements in the most external layer. To transform this ARXPS information in concentration vs depth, an iterative protocol based on the maximum entropy method (MEM) (2) can be applied.

In this work the depth profile of a S-functionalized copper sample, before and after rubbing in a tribometer was reconstructed applying MEM. The functionalization of copper with sulfur lead to the formation of Cu(I) – S bonds. The curve fitting of CuLMM (Figure 1a) allowed quantifying the % of Cu2p due to metallic copper and to Cu (I) in order to obtain the apparent concentration graph, which is the input for the MEM routine. The in depth distribution obtained is shown in Figure 1b.



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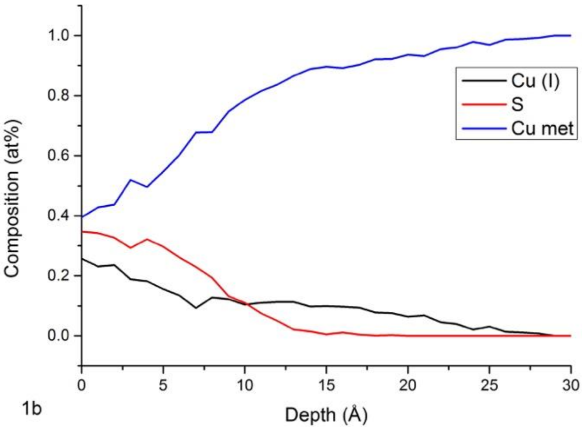

1b

Results obtained also on the in depth reconstruction of the oxide layer on the surface of brass alloys aged in buffer phosphate solution at pH 7 will be presented and discussed.

References:
1. F. Cocco, B. Elsener, M. Fantauzzi, D. Atzei, A. Rossi, Nanosized surface films on brass alloys by XPS and XAES (2015) RSC Advances, 6, 31277-31289.
2. M. A. Scorciapino, G. Navarra, B.Elsener, A. Rossi, Nondestructive Surface Depth Profiles from Angle-Resolved X-ray Photoelectron Spectroscopy Data Using the Maximum Entropy Method. I. A New Protocol (2009) J. Phys. Chem. C, 113, 21328–21337

Integrated Approach for the Chemical Characterization of Archaeological Woods

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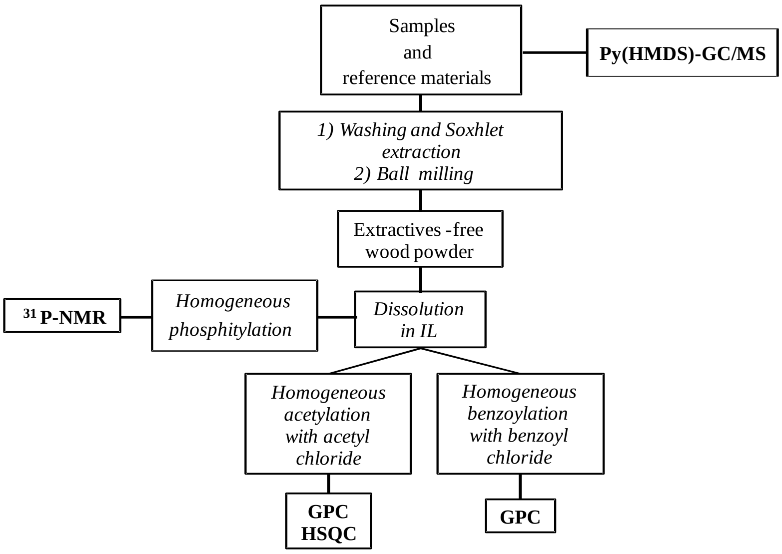
Wet archaeological wooden artefacts represent a conservation challenge still far to be solved, especially when archaeological wet wood has been previously treated with unstable materials and/or contain unstable inorganic salts which influence the degradation pathways. In order to evaluate the state of conservation of archaeological wet wood we have developed since 2007 an integrated analytical approach based on NMR spectroscopy, Py-GC/MS, and GPC analysis and applied on woods from the Site of the Ancient Ships of San Rossore (1,2,3) (Pisa Italy) and Vasa (4). Recently we have improved the analytical approach by dissolving archaeological wood into ionic liquids (ILs) as non-derivatizing solvents: in fact 1-allyl-3-methylimidazolium chloride ([amim]Cl) can provide a homogeneous reaction medium for derivatization of wood-based lignocellulosic materials. As a result, the functionalised wood developed an enhanced solubility in molecular solvents, thus enabling information about modifications of lignin, depolymerisation of cellulose and structure of lignin-carbohydrate complexes to be obtained by means of spectroscopic (2D-HSQC-NMR and ^{31}P-NMR) and chromatographic (Gel Permeation Chromatography) techniques. Py-GC-MS was used to investigate the degradation undergone by the lignocellulosic components on the basis of their pyrolysis products, without any pre-treatment of the samples [Figure 1].



The application of all these combined techniques provided a comprehensive characterisation of the whole cell wall of archaeological wood and the evaluation of its state of preservation. These analytical techniques were applied in an integrated way for the first time on archaeological wood from the Oseberg collection. High depletion of carbohydrates and high extent of lignin oxidation were highlighted in the alum-treated objects, whereas a good preservation state was found for the untreated wood of the Oseberg ship (Norway) (5).

References: 1. Colombini MP, Orlandi M, Modugno F, Tolppa E-L, Sardelli M, Zoia L. Archaeological wood characterisation by PY/GC/MS, GC/MS, NMR and GPC techniques. Microchem J. 2007;85(1):164-73. 2. Colombini MP, Łucejko JJ, Modugno F, Orlandi M, Tolppa E-L, Zoia L. A multi-analytical study of degradation of lignin in archaeological waterlogged wood. Talanta. 2009;80:61-70. 3. Salanti A, Zoia L, Tolppa EL, Giachi G, Orlandi M. Characterization of waterlogged wood by NMR and GPC techniques. Microchem J. 2010;95(2):345-52. 4. Zoia L, Salanti A, Orlandi M. Chemical characterization of archaeological wood: Softwood Vasa and hardwood Riksapplet case studies. Journal of Cultural Heritage 2015 16(4) 428-437. 5. L. Zoia, D. Tamburini, M. Orlandi, J,J. Łucejko, A. Salanti, E-L. Tolppa, F. Modugno, M. P. Colombini. Chemical Characterisation of the Whole Plant Cell Wall of Archaeological Wood: an Integrated Approach. Analytical and Bioanalytical Chemistry (2017) doi:10.1007/s00216-017-0378-7.

Assessment of nano-TiO_2 colloidal stability in aqueous media by analytical techniques and principal component analysis

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TiO_2 NPs are one of the most important inorganic materials which deserves careful investigation because of the high production and use in a wide range of applications and consumer products. In this framework, the colloidal stability assessment of TiO_2 NPs was performed varying in a controlled way the organic surface modifiers, electrolyte concentrations, pH and dispersion media. Functionalization was achieved by exploiting ligands with suitable geometries to get covalently linked to the TiO_2 NPs surface. Specifically, four catecholate derivatives (catechol, 3,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, dopamine hydrochloride), salicylic acid and polyethylene glycol (PEG) polymer were employed. Surface charge, hydrodynamic diameter and sedimentation velocity of the different NPs at two electrolyte NaCl concentrations (1 and 10 mM) were measured. The overall results were combined to obtain different dispersion stability classes, displayed by principal component analysis (PCA). The role of the organic modifiers on colloidal stability was highlighted, showing the influence exerted by NaCl concentration and pH. Under these conditions, 3,4-dihydroxybenzoic acid led to the most stable functionalized TiO_2 NPs dispersions. The study was further extended to organic and other aqueous media, i.e. ethanol, deionized water, and reference ecotoxicological media. Despite of the general destabilization observed in media with different ion valences and high salt concentrations (ionic strength up to 630 mM), an improvement of functionalized TiO_2 NPs colloidal stability was shown with respect to the pristine.

Thallium speciation in acid mine drainages, surface and tap water: A case study from northern Tuscany, Italy

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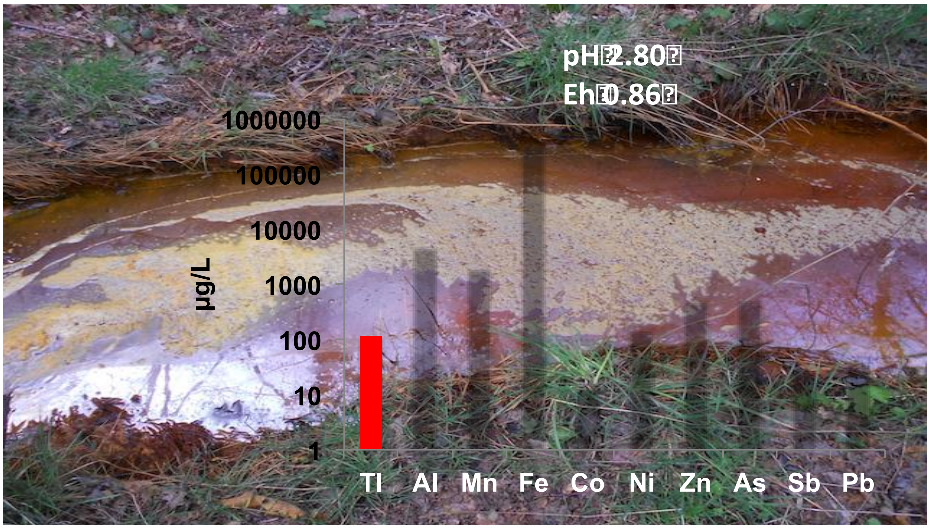
The increasing presence of thallium in the environment is attracting some attention because of its growing demand by modern high-technology industries. Thallium is more toxic than mercury, cadmium, copper, lead, and zinc, and its aquatic toxicity is apparently not affected by water hardness or humic acid concentration.

Tuscany (Italy) was one of the Italian regions that experienced a significant mining activity, which left a legacy of environmental problems related to acid mine drainages. The finding in 2014 of high Tl concentrations in drainages from abandoned mining districts located in the northwest of Tuscany (Valdicastello Carducci) posed some concern related to the potential dispersion of this element in the environment. The study of thallium redox speciation appears a way to understand its environmental behavior, since the valence state of thallium determines its toxicity, distribution and mobility.

In this work, the speciation of thallium in acid mine drainages, surface and tap water in the mining catchment of Valdicastello Carducci was first determined after separation with ion chromatography and online detection with ICP-MS. The method proposed for Tl speciation is simple, specific and fast (separation in less than 2 min). Thallium(III), considered the most unstable and toxic form of Tl, has been found in considerable amounts in drinking and river water, and it was also revealed in water samples collected in 2007.

Successively, adopting as model real water samples collected from a mine drainage and a river both rich in thallium, the distribution of aqueous Tl(I)/Tl(III) as a function of light exposure and solution properties was studied. The influence of sunlight and UV radiation, anions and organic acids was evaluated.

Beside the methodological advantages of the speciation method, our study offers a remarkable application on real samples from a thallium-contaminated area in Italy, which represents a unique possibility to investigate the behaviour of this interesting element. The study can provide an important scientific groundwork for the handling of thallium pollution.



Deposition of Airborne Pollutants on Plant Leaves and Role of Plant-Bacteria Interactions in Accumulation and Degradation Processes

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Phytoremediation has been shown to be an effective plant-based biotechnology for reducing and degrading indoor and outdoor airborne pollutants. Plants are known to scavenge significant amounts of air pollutants mainly by deposition on aboveground shoots. Leaf fall and runoff then transfer part of the adsorbed pollutants to soil and rhizosphere below. After uptake by roots and leaves, plants can metabolize, sequestrate and/or excrete air pollutants. Plant-associated microbes can help plants cope with stressful environments, but the extent to which they assist the removal of airborne contaminants in urban settings is yet poorly understood.

The main goal of the present project was an extensive and detailed characterization of the potential of the bacterial community in the phyllosphere/atmosphere to degrade airborne pollutants and to pose the basis for future successful applications of phytoremediation technologies to air pollution (1-3). Specifically, three sampling sites were chosen: two urban parks in Milano (MI) and Terni (TR), environmental hotspots, and Monte Martano (MM), a remote background site in Umbria. Five plant species (evergreen and deciduous) have been selected: *Cedrus deodara* (TR, MI, MM) *Platanus x acerifolia* (MI, TR), *Tilia x vulgaris* (MI, TR), *Magnolia grandiflora* (MI) and *Quercus ilex* (TR). Plant leaves were sampled twice each of the four seasons in 2016. Particulate matter (PM_{10}) was also sampled on a regular basis on all the sampling sites. Our aim was to characterize bacterial communities hosted by phyllosphere and atmosphere samples and to concomitantly quantify the leaf surface-adsorbed contaminants (polycyclic aromatic hydrocarbons, PAH, heavy metals, major ions). Moreover, the PAH degrading abilities and plant growth-promoting traits (PGPT) of culturable leaf-associated bacteria were assessed. Phyllospheric bacterial communities were taxonomically characterized by Illumina high-throughput sequencing of the V5-V6 hypervariable regions of 16S rRNA gene. Culturable bacteria (epi- and endo-phytes) were isolated on oligotrophic and copiotrophic media, identified through Sanger sequencing of 16S rRNA and screened for plant growth-promoting traits and ability to utilize PAHs. PAHs (39 chemical species) were extracted from leaf surface and analysed in HRGC-MS. Heavy metals have been characterized by ICP-AES and major ions by ion chromatography. The experimental database has been investigated with state-of-the-art statistical techniques.

We found that different plant species hosted specific bacterial communities. All communities were able to catch and degrade airborne pollutants, but specific patterns of activity varied among species. Most bacterial taxa were typical air-borne or plant-associated bacteria, albeit urban air pollutants are suspected to selectively reshape the composition of phyllosphere communities.

Detailed results will be discussed at the conference.

References

1. I. Gandolfi, C. Canedoli, V. Imperato et al. 2017. Diversity and hydrocarbon-degrading potential of epiphytic microbial communities on Platanus x acerifolia leaves in an urban area – Environ Pollut 220, 650-658; **2.** S.Covino, C. Casagrande, E. Ceci, et al. - Characterization of microbial communities and airborne contaminants associated to *Quercus ilex* phyllosphere in an urban environment, 14th Symposium on Bacterial Genetics and Ecology 4–8 June 2017 • Aberdeen, Scotland; **3.** I.Gandolfi, I. Rossi, et al. , FEMS 2017, 7th Congress of European Microbiologists, July 9-13 2017, Valencia, Spain.

Sito di monitoraggio in alta quota nelle Dolomiti Bellunesi (Col Margherita): sistema informatico per la gestione automatizzata dei dati meteo-climatici

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L'Istituto per la Dinamica dei Processi Ambientali (IDPA) del CNR gestisce un sito di misura di alta quota (Hight Altitude Station - HAS) in un'area remota a Col Margherita. La stazione di monitoraggio, accessibile dal passo San Pellegrino e dal passo Valles, situata nelle Dolomiti bellunesi a 2530 m sul livello del mare (latitudine 46° 22' 2.11" N, longitudine 11° 48' 23.03" E), è stata installata nell'estate del 2012 nell'ambito del progetto EU - FP7 Global Mercury Observation System (GMOS).

Per risolvere le problematiche legate alla gestione a distanza degli strumenti si è resa necessaria l'adozione di specifiche tecnologie hardware-software (IT) per l'acquisizione, gestione, trasmissione e validazione dei dati forniti dalla strumentazione automatica in dotazione alla cabina. Il sistema IT è stato progettato e sviluppato per permettere il controllo degli strumenti di misura di parametri chimico-fisici, della sensoristica meteo - climatica, delle telecamere interne/esterne della stazione.

Sviluppato su architettura Gnu-Linux, è stato utilizzato principalmente software Open Source. Sono stati integrati protocolli di comunicazione seriale per il controllo degli strumenti. L'acquisizione e la validazione dei dati viene gestita con LabView e Python. La sincronizzazione e il backup sono gestiti con Bash, crontab, scp e rsync. L'analisi statistica, la visualizzazione dei dati e la reportistica automatica sfruttano gli strumenti R, Shiny, Sweave e Latex.

Sono state considerate differenti soluzioni per la conservazione dei dati in rete (Cloud Storage) e per rendere fruibili i dati ad altri gruppi di ricerca, in accordo con gli standard Open Geospatial Consortium (OGC).

Attualmente il sito di misura è dotato di strumentazione meteo - climatica, di un analizzatore di mercurio atmosferico (TGM) e di ozono ed è in grado di integrare ai dati raccolti in automatico le misure di parametri chimico fisici ottenuti da campagne di monitoraggio hot-spot (inquinanti organici e inorganici nelle deposizioni atmosferiche, particolato atmosferico e neve).

L'obiettivo è realizzare la completa automazione dei processi di acquisizione, trasmissione, visualizzazione, validazione e produzione di report automatici dei dati misurati.

The Environmental Performance of Natural Defatting Products Used in the Leather Tanning Cycle

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The tanning industry in the EU is committed to a sustainable development at social and environmental level. The EU tanning sector is about 15-16% of the total EU leather industry, 700,000 Tons of leather and 1,800 companies mainly located in Italy (1,200-1,250) and Spain. It is fundamental to provide these industries with innovative and eco-friendly leathers that meet the EU quality standards. The crisis, which the leather sector is suffering from the reduction of internal demand and competition of low-wage third countries, is pushing for the introduction of new strategies, to address the market with innovative products and sustainable perspectives.

In recent decades, ethoxylated derivatives of fatty alcohols, vegetable oils and sugars have replaced the well-known chlorinated paraffins and alkylphenols, because of their toxicity. However, the production of ethoxylated alcohols, although profitable, may have a considerable environmental impact, since it is based on the consumption of petroleum, natural gas, animal fat and plant oils as primary raw materials.

This study, carried out under an European project (LIFE13 ENV/IT/000470 - Ecodefatting), aims to introduce new formulations in a view to reduce the environmental impact of the manufacturing processes (1). The new formulations include substances derived from natural products (lactose and citric acid) obtained in compliance with the REACH regulation (Regulation EC No 1907/2006).

The Life Cycle Assessment (LCA) methodology was applied from a "*cradle to the gate"* perspective and considering a laboratory scale production. The functional unit is the amount of the defatting agents obtained from the synthesis that is 3200g. The study was performed using the SimaPro 8.0.4 software and IMPACT2002+ impact assessment methods (2,3).

Primary data obtained from the experimental procedure were directly collected. The remaining data were obtained from specialized databases (Ecoinvent v3) and literature such as devices, machineries, plants, internal transports, ordinary maintenance operations and all data regarding installation, use and end of life steps. In addition, an environmental evaluation from the mere chemical point of view was also performed by means of the software EATOS (Environmental Assessment Tool for Organic Syntheses) (4). The use of EATOS allowed a first approximate quantification of the most impacting chemicals employed in the synthetic preparation of the degreasing product, while LCA methodology allowed to consider several further impact categories, including transportation and energy consumptions, thus realizing a more complete environmental assessment.

References
1. Pellegrini, D., Corsi, M., Bonanni, M., Bianchini, R., D'Ulivo, A., & Bramanti, E. Study of the interaction between collagen and naturalized and commercial dyes by fourier transform infrared spectroscopy and thermogravimetric analysis. Dyes and Pigments, 2015, 116, 65-73; **2.** Pré consultants, Simapro 8.04. Amersfoort, 2014, The Netherlands; **3.** O. Jolliet, M. Margni, R. Charles, S. Humbert, J. Payet, G. Rebitzer, R. Rosenbaum, IMPACT 2002+: A new life cycle impact assessment methodology, Int J Life Cycle Assess, 2003, 8, 324-330; **4.** Environmental Assessment Tool for Organic Syntheses, EATOS, user manual version 1.1, by M. Eissen and J.O. Metzger, available online free of charge at http://www.metzger.chemie.uni-oldenburg.de/eatos/eatosmanual.pdf.

Aerosols along vertical profiles: an overview of ten years of research from Italy to the North Pole

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The knowledge of vertical distribution of particulate pollution is fundamental in understanding the interplay between chemical and dynamical processes occurring within the atmosphere which finally reflects on the impact of atmospheric pollution on human health and climate change.

At this purpose from 2005 vertical profiles measurements were carried out using a unique sampling platform consisting of a tethered balloon (4.5 m diameter) equipped with an instrument package of: 1) a micro-Aethalometer AE51 (Magee Scientific), 2) a 1.107 Grimm OPC (0.25-32 µm, 31 size classes), 3) a cascade impactor (Siuotas SKC), 4) Tedlar bags for VOC, 5) a miniaturized nanoparticle detector (miniDiSC) and 6) a meteorological station (LSI-Lastem),

Tethered balloon measurements were conducted both over Italy (2005-2016; Po-Valley, Central Italy, Alpine Valley) and over Svalbard (2011-2012; Ny-Ålesund, 1200 far from North Pole) along different seasons winter, spring and summer. In addition to these, tower building based sampling activities of PM_{10} and $PM_{2.5}$ were carried out in the centre of Milan.

Aerosol samples were analysed using ion chromatography (Dionex ICS-90 and ICS-2000), GC-MS (Agilent 6850 and 5973), SEM-EDS (Philips XL30).

The aims of the aforementioned campaigns were to determine the aerosol chemical composition with height in relationship with size distribution data in order to investigate the aerosol dynamics across the Planetary Boundary Layer (PBL) as driver for important feedbacks on human exposure to PM (ground-level concentrations) and on climate change (feedbacks induced by the atmospheric heating and aerosol vertical location).

All the collected data (Italy and Svalbard) indicated the top of PBL as a clear transition in aerosol chemical composition, concentration and size distribution.

On the Italian side, coarse particles experienced a lower atmospheric mixing than fine particles due to settling processes, leading to a decrease with altitude of crustal components (i.e. Ca^{2+}, silicates); at the same time, fine particles experience an increase of their size together with secondary aerosol components (i.e. ammonium nitrate), sphericity, and correlation among fine aerosol sizes. This pattern evidenced recurrent ageing dynamics (condensation/coagulation) (1). In this respect, experimental results were coupled with modelling activity (WRF-Chem) (2), clearly showing that secondary aerosol formed in upper aerosol layer is of great importance as may contribute up to 25-40% to ground level concentrations on an hourly basis affecting human exposure.

Moreover, a ground-level layer of black carbon (BC; from +16.1% to +34.2%) was evidenced in according with a ~30% higher content of polycyclic aromatic hydrocarbons with respect to the whole PBL. BC also revealed a marked concentration drop across the PBL (from -48.4±5.3% up to -69.1±5.5%) resulting in a heating rate characterized by a vertical negative gradient (from -2.6±0.2 K day^{-1} km^{-1} up to -8.3±1.2 K day^{-1} km^{-1}) able to promote a negative feedback on the atmospheric stability (3).

On the Svalbard side, results allowed to describe for the first time the seasonal phenomenology of vertical aerosol properties allowing to discover a springtime low-altitude secondary aerosol formation (enriched in sulfates) never observed before in that area (4).

Most important, the mid-latitude (Italy) – North Pole (Svalbard) comparison of vertical behaviour of BC allow to experimentally interpret the modelling explanation of the Arctic Amplification (double heating compared to the globe).

References

1. Ferrero et al., Atmospheric Environment 56 (2012) 143-153; **2.** Curci et al., Atmos. Chem. Phys., 15, 2629–2649, 2015; **3.** Ferrero et al., Atmos. Chem. Phys., 14, 9641–9664, 2014; **4.** Ferrero et al.., Atmos. Chem. Phys., 16, 12601–12629, 2016.

Radioactivity in Domitia coastal area (Southern Italy): a multidisciplinary approach

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Aim of this work is the radioactive characterization of two Campanian coastal environments, in particular down drift the river discharges, that had never been examined before, in order to investigate the distribution vs depth of natural (^{238}U, ^{232}Th, ^{226}Ra, ^{40}K) and anthropogenic (^{137}Cs, ^{239}Pu, ^{240}Pu) radionuclides and their handling in the coastal environment. Samples were collected down-drift the Garigliano river mouth, to understand if the Garigliano Nuclear Power Plant (GNPP) located near the edge of the river, could represent a source of contamination. For comparison, an analogous coastal site has been chosen southward, down-drift the Volturno river, far enough from the GNPP, otherwise contaminated (1). Natural and anthropogenic gamma emitters were analyzed by γ-Ray Spectrometry. Moreover, stratigraphic and sedimentological characterization has been carried out on the cores first by identifying their sedimentary pattern, the fossil content and by their description in stratigraphic logs, then by wet-sieving and selection of mollusca shells for ^{14}C dating by AMS (Accelerator Mass Spectrometry). In order to investigate the mineral composition, we have adopted the WAXRD (Wide Angle X-Ray Diffraction) technique. Since sandy matrices had never been analyzed before in our laboratory, except for soils and concrete (2), with only a scarce literature existing about their treatment, a new protocol (3) was realized by us to detect the anthropogenic ^{239}Pu, ^{240}Pu. This method can be simplified in two phases: the pre-concentration phase and the column separation. In the first phase, the sample is sieved, dried, combusted, leached and concentrated through steps of iron precipitation, centrifugation and washing. The second phase comprises: i) an anion-ion exchange resin for the extraction of Pu with other impurities, ii) its purification with the TEVA® Resin and iii) its detection by ICP-MS. As experimentation, this procedure has been extended by us, also to the analysis of samples by AMS: a part of the solution obtained after the final treatment is subjected to another cycle of iron precipitation and washing~~s~~ to reduce the volume, subsequently, it is dried and baked at 800°C for 8 hours and analyzed by AMS. This multidisciplinary approach has provided new important insights on the sedimentary evolution of the two deltaic strand plains studied, as well as on the detection and interpretation of the radionuclide content in coastal sandy matrices. The consistent presence of natural radionuclides is due to the volcanic and sedimentary rocks; ^{137}Cs does not contribute to the contamination of the coastal areas; the analytical procedure adopted to extract anthropogenic Pu by sand with ICP-MS is applicable to AMS detection. The ratio is set in the typical range of the global fallout (the Chernobyl accident), allowing the GNPP to be excluded from the contamination of the coast.

References
1. Verde R., Vigliotti M., Prevedello L., Sprovieri M., Ruberti D., (2013), An integrated approach to environmental quality assessment in a coastal setting in Campania (Southern Italy) Environ Earth Sci, 70:407–424, DOI 10.1007/s12665-012-2136-7; **2.** De Cesare M., PhD Thesis, (2009), Accelerator Mass Spectrometry of actinides at CIRCE; **3.** Qiao j., PhD Thesis, (2011), Rapid and automated determination of plutonium and neptunium in environmental samples.

Single particle characterization of particulate matter: Source apportionment

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An air environment includes solid and/or liquid particles in a variety of elements and shapes and gas component. Short-term and long-term exposure to elevated concentrations of these aerosol particles is associated with a number of adverse health effects as for example lung cancer, inflammatory lung disease, respiratory diseases, cardiovascular diseases and premature death. The aerosol particles are emitted by a wide variety of emission sources and can be transported over vast distance. Therefore, to devise a means of control, it is important to monitor the pollution level of particulate matter and to discover the type of emission sources by receptor model. The conventional source apportionment methods are based on bulk chemical analysis and require the specification of emission sources and information on the elemental composition of particles from each of the emission sources. In this work, we applied individual particle analysis to sources apportionment of particulate matter using scanning electron microscopy coupled with energy dispersive analysis (SEM-EDS) (1). This approach is based on the hypothesis each aerosol particle can deliver unique information about its emission source. Based on the morphology and chemical composition determined by scanning electron microscopy and energy-dispersive X-ray microanalysis, the particles were classified into the following fourteen groups: alumosilicates, silicates, calcium sulfates, sulfate-silicates mixtures, carbonaceous particles, soot, biological particles, sea salt, iron oxides, iron mixtures, metal oxides, secondary particles, fluoride and calcium carbonates. The particle groups observed in the present work can be assigned to different emission sources. Source apportionment based on properties of individual particles is especially helpful for discrimination of industrial emissions originating from high temperature processes from a natural soil component (2). The following source categories were distinguished and apportioned: soil, industry, secondary, soot, carbonates, calcium sulfates, sea salt and other.

References

1. A Genga, F Baglivi, M Siciliano, T Siciliano, M Tepore, G Micocci, C Tortorella, D Aiello, SEM-EDS investigation on PM10 data collected in Central Italy: Principal Component Analysis and Hierarchical Cluster Analysis, Chemistry Central Journal 6 (2012) suppl2 S3; **2.** M. Ebert, D.M. Ebert, N. Benker, S. Weinbruch, Source apportionment of aerosol particles near a steel plant by electron microscopy, J. Environ. Monit., 2012, 14, 3257-3266.

Quanto mercurio nelle acque minerali naturali della Campania?

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Il mercurio (Hg) è un inquinante ubiquitario prodotto da sorgenti antropiche e naturali, con effetti negativi sugli ecosistemi e sulla salute umana. La provenienza di questo metallo pesante oltre ad essere locale e regionale è anche transfrontaliera. Per tale motivo nel 2013, attraverso la Convenzione di Minamata, 140 paesi (di cui 26 dell'Unione Europea) hanno sottoscritto il Trattato che fissa la riduzione e il controllo dell'impiego di Hg in prodotti e in processi industriali e artigianali (1) per garantire la protezione dell'ambiente e della popolazione. Una volta immesso nell'ambiente il Hg, attraverso processi batterici naturali, viene trasformato in mono-metil-mercurio (MeHg) in ambienti acquatici. Il MeHg è il più tossico dei composti organo-mercuriali e data la sua elevata liposolubilità va incontro a bio-accumulo e bio-magnificazione (2). Oltre che con gli alimenti, il Hg può essere assunto con l'acqua, anche se in misura inferiore (3). Studi condotti su scala internazionale hanno evidenziato che monitorare le concentrazioni dei macro-elementi caratteristici, di metalli tossici e di specie indesiderate nelle acque in bottiglia permette di valutare non soltanto la qualità dell'acqua, ma anche lo stato di salute delle falde e di comprendere la geochimica delle acque sotterranee (4). Nelle pubblicazioni più recenti sono stati forniti dati relativi a numerosi parametri chimici e metalli pesanti, ma tali lavori sono privi di informazioni sui livelli di Hg (4, 5), in quanto i valori ottenuti sono risultati inferiori ai limiti di quantificazione del metodo analitico impiegato.

Figura 1 - Acque in bottiglia in laboratorio.

Figura 2 - CV-AFS.

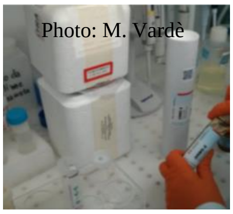

Figura 3 – CRMs.

Un totale di 19 differenti acque minerali provenienti da acquiferi della Campania e reperite sul territorio nazionale, sono state analizzate per valutare l'eventuale presenza di mercurio (Fig. 1). Prestazioni analitiche ottimali, in termini di controllo di possibili interferenze e limite di rilevabilità, sono state ottenute impiegando la spettrometria di fluorescenza atomica a vapori freddi (CV-AFS), consentendo la determinazione del mercurio totale a sub-ppt (Fig.2). Questa specifica tecnica strumentale unita alle accortezze adottate nella metodica analitica, l'impiego di matrici certificate e la partecipazione a circuiti di inter-comparazione internazionale (Fig.3) si sono dimostrate idonee per la rigorosa valutazione delle concentrazioni di mercurio, altrimenti non raggiungibili con strumentazione come AAS e ICP-MS. I risultati presentati in questo lavoro indicano che i livelli di Hg sono ampiamente al di sotto dei limiti legislativi e dunque l'assunzione di Hg in ultra-tracce con le acque minerali naturali non pone rischi per la salute umana.

References

1. http://www.mercuryconvention.org; **2.** Global Mercury Assessment (2013): Sources, Emissions, Releases, and Environmental Transport. UNEP, 42; **3.** WHO "Mercury in drinking-water" – WHO/SDE/WSH/05.08/10, 2005; **4.** Birke et al., J Geochem Explor 107 (2010) 217–226; **5.** Cicchella et al., J Geochem Explor 107 (2010) 336–349.

Efficiency improvement of the TiO_2 – ZnO NPs photocatalytic coupled system supported on a persistent luminescence material

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Heterogeneous photocatalysis is applied to several research areas, especially for environmental applications; among these, water remediation and wastewater bleaching are important fields the scientific research is focusing on. TiO_2 and ZnO (NPs) are the most preferable materials, due to their excellent chemical stability, high carrier mobility, environmental sustainability, high photocatalytic efficiency, nontoxicity and low cost for massive synthesis. However, TiO_2, as much as ZnO, are limited as sunlight-driven photocatalysts, due to their large band gap (ca. 3.2 eV for both), which requires, for photo-activation, photons with energy at least equal to the band gap; hence, the UV light source is mandatory (UV represents only 5-8% of the solar spectrum). A possible way to overcome this limitation is using a supporting material, capable to emit a proper radiation in order to activate "internally" the photocatalyst. It was reported as supporting the photocatalyst onto a persistent luminescence material (PeLM) increased the general efficiency and allowed the photocatalytic process to occur even in the darkness. In fact, the PeLM is able to be charged with both natural and artificial radiation and, glowing in darkness, provides the necessary photons to the catalyst (1). The coupled system has potential application in the removal of organic emerging pollutants, being particularly effective in the treatment of contaminated water by pharmaceutically active compounds and in turbid wastewater like olive mill vegetation waters. Both the matrixes are characterization by poorly biodegradable products. The capability to work also in darkness is significant in the reduction of electric energy consumption, resulting, in principle, to be an energy neutral technique for water purification and pollution control. The coupled system was obtained through a solid state synthesis: amorphous TiO_2 powders (synthesized *via* sol-gel technique), ZnO powders (2) and PeLM powders (prepared *via* solid-state synthesis) were mixed in water under magnetic stirring for 30 minutes, dried in oven at 105 °C for 12 hours and eventually subjected to a thermal treatment at 350°C for 1 hour. Several samples were prepared, by varying the weight ratio between the reagents powders, and characterized by means of XRD, SEM, BET. The photocatalytic activity was evaluated using a methylene blue solution. The best catalysts were then tested on a turbid solution of olive mill wastewater and an aqueous solution contaminated with pharmaceuticals compounds, e.g. the fluoroquinolone antibiotic Ofloxacin.

References

1. Locardi F.; Sanguineti E.; Fasoli M. *et al.* Catalysis Communications 2016, 74, 24-27; **2.** Lova P.; Manfredi G.; Boarino L. *et al*, Physica Status Solidi (c) 2015, 12 (1-2), 158-162.

Thermal processing alternative of biomass residue for biochar applications

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Efficient and innovative valorization of digestate from anaerobic digestion (AD) is one of the key issues for the development of sustainable biorefinery schemes based on bioenergy and bioproducts. Digestate contains several nutrients that should be returned to the fields, but its exploitation in agriculture sometimes constrained by to various factor, such as risk of N leaching and water eutrophication (see “Direttiva Nitrati”). Thermal treatment through pyrolysis or hydroprocessing can be considered as an alternative pre-treatment step to stabilize the solid digestate from AD. Carbonized (and thus sterilized) solid digestate is an easily transportable high added-value product, also called biochar. The present study reports on the results of two digestate carbonization experiments carried out in distinct processes at lab and pilot-scale: conventional carbonization (slow pyrolysis, SP) and hydrothermal carbonization (HTC). The digestate was obtained by a 1 MWel plant located in Italy, and derived from the anaerobic digestion of agro-industrial residues and herbaceous biomass. The sample was characterized by proximate and ultimate analysis, determining macroscopic parameters such as moisture content, ash, volatile substances and higher and lower heating value and elemental composition (CHNS), including inorganics. In order to process the feedstock in the slow pyrolysis reactor, the digestate was dried at 75 °C for 48 hours in order to reduce its high water content (76.2% w/w w.b.). Preliminary ThermoGraviMetric (TGA) allowed the determination of the devolatilization behavior and the solid residue (27.8% w/w d.b. at 900°C).

The slow pyrolysis was carried out in a batch stirred reactor, under a 10 l/min N_2 flow, at an average heating rate of about 7 C°/min, and the maximum process temperature of about 500 °C was maintained for 1 hour.

Due to the high water content of the digestate, HTC is a very promising process for the direct utilization of these wet feedstocks, without any pretreatments, differently from pyrolysis that requires very dried material at inlets. HTC represents a very innovative technology, capable of directly exploiting wet feedstock by avoiding the energy-intensive step of drying. HTC experiments were performed in a micro reactor in batch mode at 10% w/w biomass to water ratio, investigating different reaction temperatures (200-250°C) and residence times (0.5-3 h). Mean heating rate ranged between 33.5 to 43.0 °C/min.

The products obtained from the slow pyrolysis and hydrothermal carbonization of digestate were characterized and compared in terms of ultimate, proximate and BET analysis. Furthermore, the HTC aqueous phase was analyzed by means of gas chromatography and HPLC techniques.

In the HTC experiments the carbon content of the char and its yield showed an opposite trend: by increasing reaction severity, in terms of temperature and residence time, the yield decreased and the carbon content increased. As far as the slow pyrolysis process is concerned, its yield was substantially lower than the HTC cases, thus indicating a higher carbonization degree, as confirmed by the analysis of the product

In addition, other specific analyses were also carried out, comparing the obtained chars with the current Italian and international product standards in order to assess their potential commercialization and limits as a potential amendment in agriculture, with benefit for the entire AD chain.

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Catalytic oxidation of trichloroethylene over mayenite: Influence of the preparation method on the catalytic activity

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Trichloroethylene (TCE) is a chlorinated solvent that belongs to the class of dense non-aqueous phase liquids, and it is an ubiquitous environmental pollutant (1). Thermal and catalytic routes were investigated as valuable techniques to TCE complete destruction (2). The activity of mayenite in the catalytic oxidation of chlorinated organic compounds was recently investigated obtaining interesting results (3). In this work mayenite was synthesized by different routes namely ceramic (Cer), Sol-gel (Sg) and hydrothermal (Hydro). The synthetized catalysts have been evaluated for the oxidation of trichloroethylene by monitoring the conversion as function of the temperature (light-off curve). Experiments were carried out at atmospheric pressure in a fixed bed reactor.

As shown in Tab.1, Mayenite prepared by the Hydrotermal method showed better performance (T_{50}= 350 °C, T_{90}= 500 °C) in absence of water than the other mayenites. The effect of water vapor on the TCE catalytic oxidation was also investigated. The results showed that the addition of water to the feed stream did not alter the activity observed except for mayenite prepared by the ceramic route. These differences in catalytic activity could be explained by the different surface area of the catalyst. Mayenite prepared by Hydrotermal route presents the highest surface area (MayeCer = 11.7 m^2g^{-1}; MayeSg= 2.0 m^2g^{-1}; MayeHydro = 35.5 m^2g^{-1}) and the highest activity. In literature its proposed that the activity of the mayenite is related to the presence of $O^{2-}$and O_2^{2-} anions sites that favour the total oxidation of TCE (4). It seems that the mayenite synthetized by the hydrothermal method has a good combination of surface area and redox properties that explain the great activity of this material in the TCE oxidation reaction.

T	Blank	Maye Cer	Maye Hydro	Maye Sg
150	0	0	0	0
200	0	0	6	0
250	0	0	11	8
300	0	4	17	10
350	0	18	48	31
400	0	30	85	54
450	0	51	87	57
500	0	75	93	70
550	10	85	100	86

Tab. 1 TCE conversion in dry conditions for Ceramic Mayenite, Hydrotermal Mayenite, Sol-gel Mayenite ([TCE]= 1000 ppm, 400 mL/min, 0.7 g of catalyst)

As conclusion, we can state in order to obtain an active catalyst for the TCE oxidation, we need a combination of oxidative properties and high surface area. Those can be obtained preparing a mayenite with the hydrothermal route due to lowest temperatures used in this method for the preparation of the catalyst. Moreover except for Ceramic mayenite, it was showed that the presence of water did not increase the activity of the materials.

References

1. F. Rossi, R. Cucciniello, A. Intiso, O. Motta, N. Marchettini, A. Proto (2015) AIChE J. 61, 3511-3515; **2.** N. Blanch-Raga, A.E. Palomares, J. Martínez-Triguero, S. Valencia (2016) Appl. Cat. B: Environ. 90–97; **3.** R. Cucciniello, A. Intiso, S. Castiglione, A. Genga, A. Proto and F. Rossi (2017) Appl. Cat. B: Environ 204, 167-172; **4.** M. Teusner, R.A. De Souza, H. Krause, S.G. Ebbinghaus, B. Belghoul, M. Martin, (2015) J. Phys. Chem. C 119, 9721–9727.

Clear evidence of the Macromolecular Structure of Humic acids

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The Humic substances (HS), a class of compounds obtained from biological decomposition of the organic matter, play an important role in the environment. They are the main fraction of the soil organic matter, and are of paramount importance in sustaining plant growth. HS are responsible for the structure and physico-chemical properties of soil and are involved in the majority of soil surface phenomena. In function of their solubility in water, they are divide in umina, humic acids (HA) and fulvic acids. HA are the fraction soluble at neutral and alkaline pH and are the main carriers affecting the mobility of pollutants in the environment. Because of their role, HS have been object of many scientific reports about their chemical structure and adsorbing property. They have aromatic structures and alkyl chains with a diversity of functional groups, notably carboxyl, phenol, hydroxyl, and quinone groups. In water HA molecules tend to aggregate giving colloids (1). Self-assembly increases with concentration, at low pH and in the presence of metal ions. Because of this and of the wide mass distribution of HA, an accurate determination of the molar mass of these compounds is a difficult task. Despite the large number of scientific reports, their molecular mass still remains unclear and is the object of an intense current debate in literature. Same researchers have suggested in recent years that HA consist of small unites that are held together by weak intermolecular forces (2): a supramolecular assembly.

This communication deals with a study on the molecular structure on three samples of HA: a) extracted from leonardite (3) a vitreous mineraloid product formed by natural oxidation of lignite and mined in many countries; b) extract from compost (3); c) a commercial sample, obtained from the decomposition of dead plants and supplied by Alfa Aesar (Germany). The molecular structure was investigated by treatment with the monocarboxylic acids, dialysis experiments and size-exclusion chromatography (SEC). SEC experiments at low pressure gave chromatograms with a broad peak, with an elution volume at the maximum height of the peak very close to that of the globular protein bovine serum albumin, molar mass = 66.5 kDa. The pattern of the chromatogram did not vary with HA concentration, and second-run chromatograms of single eluted fractions showed relatively sharp peaks. Moreover, HA molecules were retained by dialysis membrane with cut-offs of 6 - 8 kDa. From these data, it seems that the HA in the samples analysed have a canonical macromolecular structure rather than being a supramolecular aggregate of relatively small molecules, as recently proposed.

References
1. Jones, M. N., Bryan, N. D., 1998. Colloidal properties of humic substances. Advances in Colloidal and Interface Science 78, 1-48; **2.** Piccolo, A., 2001. The supramolecular structure of humic substances. Soil Sci 166, 810-832; **3.** Leone, V., Musmarra, D., Iovino, P., Capasso, S., 2017. Sorption Equilibrium of Aromatic Pollutants onto Dissolved Humic Acids. Water Air Soil Pollution 228, 136. DOI 10.1007/s11270-017-3321-9.

Accelerated tests to evaluate the combined effect of aggressive saline components of atmospheric particulate matter on corrosion and metal release of weathering steel

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Weathering steel (WS) is a low-alloy steel which naturally develops a protective patina of corrosion products on the surface after its atmospheric exposure. The composition, stability and consequently the protective ability of the patina is strongly affected by exposure and climatic conditions, as well as by the presence and amount of atmospheric contaminants (1,2). Among them, particulate matter (PM) may interact with the exposed material enhancing its aesthetic decay and corrosion (3), with consequent release of alloying elements in the environment.

In a previous work (4) the effects of the main anionic constituents of PM (chlorides, nitrates and sulphates) on WS corrosion were studied by means of an accelerated ageing test, characterized by alternated immersion of samples in solutions with different concentrations of the single selected species. That work provided interesting information about the effect of single salts, which acted on metal corrosion with different mechanisms and kinetics, and laid the basis for a more detailed study aimed at evaluating a more realistic situation, where these species can interact and possibly produce synergistic effects in the corrosion process.

For this purpose, new wet&dry ageing tests were set up and performed using different mixtures of Cl^-, NO_3^- and SO_4^{2-}. The concentrations of each species in the mixtures ranged between 1.5 and 35 mg L^{-1}, to simulate the exposure to both mild and quite aggressive environments, and the composition of the solutions was selected through multivariate techniques (Design of Experiment). WS corrosion in presence of the different mixtures of Cl^-, NO_3^- and SO_4^{2-} was examined by analyzing corrosion rate and alloying metal release both in dissolved and particulate fractions. The study of the effects of the considered salts depending on their ratios in the different solutions appears very interesting if considering the modifications in the composition of atmospheric depositions due to present changes in air quality.

References
1. M. Morcillo, et al., Corros Sci 83, 6-31, 2014; **2.** S. Raffo, et al., Environ Pollut 213, 571-584, 2016; **3.** B. Liu, et al., Environ. Monit. Asess., 187:4112, 1-11, 2015; **4.** S. Raffo, et al., Conference Proceedings XVI SCI-ABC, Lecce, 26-29 giugno 2016.

Analysis and detection of emergent contaminants in seawater by passive sampling

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The aim of this study is to assess the performance of POCIS (Polar Organic Chemical Integrative Sampler) passive sampling for the analysis of diuron and some sulfonamides in seawater, with a critical evaluation of the analytical method of detection and quantification by UPLC-QTof. Monitoring by passive sampling (PS) is based on mass transfer due to the different chemical potentials of analytes between a given environmental compartment and the collection medium inside a dosimeter. POCIS samplers are used to sample polar hydrophilic compounds with octanol/water partition coefficients logKow<3. Two configurations are used for sampling different classes of contaminants, spanning a wide range of polarity ($0.05 \leq \log K_{ow} \leq 2.68$): pharmaceutical-POCIS (pharm-POCIS) and pesticide-POCIS (pest-POCIS). The sorbent in POCIS samplers is usually based on polystyrene divinylbenzene combined with active carbon in the case of pest-POCIS, or Oasis™ HLB sorbent in pharm-POCIS.

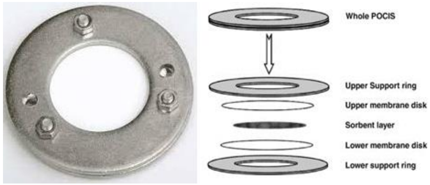

Fig.1 POCIS sampler

Pest-POCIS and pharm-POCIS laboratory calibrations have been conducted to calculate the sampling rates (Rs) of 7 polar contaminants (5 sulfonamides, diuron and trimethoprim), commonly found in seawater. Calibrations have been conducted in parallel in a double synthetic marine water system with two blank tests. Samples of water were taken at regular intervals and extracted by SPE (Oasis-HLB), until complete exhaustion. At the end, the POCIS samplers were analyzed and results were comparable to the expected values. Environmental application took place in the Gulf of La Spezia.

A selective and sensitive method has been developed for the determination of the Rs's for diuron and some sulfonamides. The results of the study allowed to obtain a fast, efficient and sensitive method of determination, able to comply with the Environmental Quality Standards (EQS) established for this analytes in the Water Framework Directive. Passive sampling is very appealing for the determination of time-weighted average concentrations and the response time of the sampler can be chosen according to the desired length of the sampling period. The main advantage of passive sample collection/enrichment technology lies in the considerable simplification of sample collection *in situ*, and it seems to be a valuable complement to generally applicable dynamic methods. Extensive laboratory calibration of POCIS samplers were performed and kinetic uptake studies were carried out without analytically complex procedures, ensuring the general applicability of the approach. Samplings from La Spezia showed that POCIS samplers compared very well with the traditional discrete sampling.

Removal of emerging organic pollutants in wastewater treatment plant effluents by an electrochemical process employing boron-doped diamond electrode

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Various studies over recent years have proved the increasing occurrence in effluent of wastewater treatment plants (WWTP)of several contaminants of emerging concern (CECs), which are not completely removed by the common technologies employed in conventional WWTP. CECs found at highest levels (ng L^{-1} to µg L^{-1}) are pharmaceuticals, artificial sweeteners, pesticides, flame-retardants, plasticizers and perfluoroalkyl substances (1,2).

The main objective of this study was to investigate an electrochemical treatment based on a boron-doped diamond (BDD) electrode, as an advanced oxidation process (AOP) for the removal of several CECs from effluent of WWTP with enhanced performance in terms of efficiency and applicability (3).

Electrochemical treatments were performed with a CONDIAPURE® system using a DIACHEM® electrode stack in a flow through cell (CONDIAS GmbH, Germany), in both synthetic water and real secondary effluent. The electrode stack was composed by two BDD cathodes and one BDD anode and in situ oxidation was performed with four anode/cathode pairs applying a total current of 0.4 A. A total of 10 L of solution with the target organic pollutants was circulated through the reactor at a flow rate of 18.5 L/min.

The removal of a mixture of CECs (iopromide, carbamazepine, diclofenac, erythromycin, benzotriazol, sulfamethoxazole, caffeine, gabapentin, metoprolol, phenythoin, primidone, venlafaxine, TCEP) by the investigated electrochemical system was primarily assessed in synthetic model water spiked with the target contaminants at concentration in the range of 2-5 µg L^{-1}. Removal below limit of quantification (LOQ) was achieved for all tested compounds after 200 min of treatment. Decay follows pseudo first order kinetics and kinetic constants (k) of 0.07 min^{-1} for sulfamethoxazole and diclofenac and in the range 0.03-0.01 min^{-1} for the other CECs were obtained, being TCEP the pollutant with slowest kinetics.

Afterwards, the secondary effluent of the municipal WWTP Garching (Germany) was employed as a real water matrix which revealed the occurrence of several CECs (including the mixture of selected compounds listed above) at concentration levels between 20 ng L^{-1} and 20 µg L^{-1}. The electrochemical treatment of the effluent was performed under the same conditions employed with the spiked synthetic water. Results demonstrated removal below LOQ for all the target CECs after 300 min with lower degradation rates than in the spiked synthetic water solution ($k \leq 0.01$ min^{-1}).

The detection of transformation products of investigated CECs was performed by UPLC-QTOF/MS/MS, by employing a non-target analysis approach which was based on accurate MS and MS/MS data and open source databases and software.

References

1. R. Loos, R. Carvalho, D. C. Antònio, S. Comero, G. Locoro, S. Tavazzi, B. Paracchini, M. Ghiani, T. Lettieri, L. Blaha, B. Jarosova, S. Voorspoels, K. Servaes, P. Haglund, J.Fick, R. H. Lindberg, D. Schwesig, B. M. Gawlik. Water Research 47 (2013) 6475-6487; **2.** S. Murgolo, V. Yargeau, R. Gerbasi, F. Visentin, N. El Habra, G. Ricco, I. Lacchetti, M. Carere, M.L. Curri, G. Mascolo. Chemical Engineering Journal 318 (2017) 103-111; **3.** M. Rajab, C. Heim, G. Greco, B. Helmreich, T. Letzel. International Journal of Environmental Pollution and Solutions, 1 (3) (2013) 88-97.

Chemical characterization of freshly emitted steel plant fumes by chemical and spectroscopical methods

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Atmospheric aerosols, emitted by both anthropogenic and natural sources, affect the climate system and the human health in many ways (1). Aerosol chemical composition can be very complex because of the multi-compounds emission at the source and the mixing and ageing processes that can happen during its permanence in the atmosphere. Industrial processes can emit many different compounds, and some of them are particularly relevant in terms of harmful potential for human health, such as heavy metals and PAHs, and climate impact, like iron and light absorbing carbon containing compounds (black carbon). Iron speciation, in particular, is a rising topic in aerosol research because it helps to determine the harmful potential of Fe-bearing particles and also their impact on oceanic and Amazonian rainforest productivity (2). In this frame, a characterization of the aerosol at the source is useful to understand which types of compounds are emitted, to trace them through their transport in the atmosphere and to assess the single source contribution to the total aerosol composition.

In this work, we characterized steel production emissions from the Thyssen Krupp (TK-AST) plant in Terni, Central Italy. This plant is located inside the urban area and its emissions are clearly detectable in the urban aerosol composition (3). We investigated the composition of aerosol emitted by two smelters and two converters. The samples were taken inside the chimney stacks of the plant in order to avoid mixing with other types of aerosol and atmospheric processing.

Both chemical composition and mineralogy were investigated by means of several analytical techniques such as Inductively Coupled Plasma Mass Spectrometer (ICP-MS), Ion Cromatography (IC), Gas Cromatography (GC) and X-ray diffraction (XRD). Moreover, a detailed study on iron speciation was performed by means of selective leaching experiments and X-ray absorption spectroscopy (XAS). Chemical analysis shows very high emissions of Fe, Ca and fluorides and evidence some differences between the different plant sections also in alkanes profile and PAH distribution. XRD analysis show three main phases, two slightly different magnetite phases and one calcite. The predominance of spinel oxide iron structure is remarkable also in the XAS results, but a different Fe^{2+}/Fe^{3+} ratio has been observed compared to the pure magnetite structure. Leaching experiments show a high predominance of the residual insoluble fraction, attributable to spinel oxides, among the others accordingly with mineralogical results, while the contribution of the other fractions is highly variable amongst the different plant portions.

References
1. Seinfeld and Pandis 2006; **2.** Mahowald et al. 2009, Annual Review of Marine Science vol. 1; **3.** Moroni et al. 2013, Rendiconti Lincei vol. 24.

Exploitation of agro-residues in designing of silicate materials

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Up to now, the agro-industrial sector is an important resource for the global economy, with very different production realities (milk and derivatives industry, slaughtering of animals and production of cold cuts, manufacturing and processing of fruits and cereal, etc.). Each type of agro-residue often contains a lot of high value-added substances that constitute a new raw material for possible applications of commercial interest. In this work, we report some case studies related to the possibility of exploiting some agro-wastes and by-products (rice husk ash, sawdust, grape seeds, cherries seeds, sugar cane ash, sludge from beer wastewater treatment plant, animal bone flour or flour ash, corn cob and olive pomace) in silicate materials (sintered and vitrified) useful for both building and agronomic sector. Ceramic bricks were obtained by introducing rice husk ash, RHA, (mainly constituted by amorphous silica and together with low amount of tridymite and cristobalite phases), (up to 20 wt%) as silica source or sawdust, grape and cherries seeds (up to 10 wt%) as pouring agents in clays mixtures. The introduction of RHA into brick bodies influences the sintering behavior, it did not affect the linear shrinkage%, while water absorption% values showed an increase as RHA content increases. From the mechanical point of view, samples with up to 5 wt% resulted satisfactory (12 MPa) comparing to the industrial limit (10 MPa). Sawdust, grapes and cherries seeds, due to their organic substances content, during their combustion, bring an energetic support in the bricks firing phase and act as pore forming agent. Grapes and cherries seeds also maintain the mechanical properties of the fired brick, showing modulus of rupture around 21–23 MPa with a weight reduction of 3–10% with respect to the standard one.

Spherical pellets of lightweight aggregates were prepared by mixing different percentages (up to 15 wt%) of sludge from beer wastewater treatment plant, animal bone flour, corn cob and olive pomace in two different clay-based mixtures and thermal treated at 900 and 1000°C for 1 hour. Technological parameters such as bulk and absolute density, total porosity, water absorption, pH and electrical specific conductivity were determined in order to test their potential use in agriculture. Animal bone flour ash was also used to formulate glass and glass-ceramic fertilizers, with a low and controlled solubility in water of macro nutrient elements useful for plants as P and K. From the preliminary results, it is possible to hypothesize poring effect in the realization of lightweight aggregates for different application fields such as lightweight substrate/soil for agricultural use, as pH corrector for acid soils, because they showed pH between 8-9. On the other hand, further tests were conducted by adding to these mixes (clay-poring agent) 10 wt% of animal bone flour ash or a fertilizer glass-ceramic (P_2O_5+K_2O > 12wt%) or calcined olive pomace. In order to verify the nutrients release of the functionalized lightweight aggregates, tests following European and Italian rules using citric acid solution (2%vol) and distilled water were performed. The results highlighted that mix containing the bone ash releases more amount of nutrient in a short time (30 min) on the contrary the compositions containing the fertilizer glass showed a high release at longer time (21 days). This aspect is important from the environmental point of view because the slow release can avoid the leaching by rain of nutrient elements and their concentration in groundwaters.

B-IMPACT: a new project for the development of eco-friendly and non-hazardous outdoor bronze protective coatings

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The B-IMPACT (Bronze-IMproved non-hazardous PAtina CoaTings) project, funded within the European M-ERA.Net consortium, aims at developing innovative eco-friendly and non-hazardous protective coatings for the protection of bronze surfaces exposed to the outdoor environment (http://www.b-impact.eu, info@b-impact.eu). This project, started in March 2015 and ended in April 2017, was coordinated by the Slovenian National Building and Civil Engineering Institute and involves academic partners (University of Toulouse (F); University of Bologna and University of Ferrara (I), together with industrial partners for bronze production (Livartis d.o.o. and Geida d.o.o. (SLO)) coating formulation (Pylote SAS and C2M Aurochs Industrie (F)) and toxicity assessment (Ecamricert SRL (I)).

Two different bronze alloys, supplied by the artistic foundry Livartis, have been considered as substrates: a modern silicon bronze (Cu-3Si-1Mn) used in contemporary art, artificially black patinated with K_2S ("liver of sulphur"), and a historical quaternary bronze (Cu-6.5Sn-4Zn-2Pb), patinated by artificial ageing in conditions which closely simulate outdoor exposure (runoff and stagnant rain conditions). The performance of protective coatings has been assessed by electrochemical tests in artificial acid rain and, in the case of the most promising ones, by severe accelerated ageing involving environmental parameters (rain runoff, UV radiation ...). Both the exposed surfaces (coated vs. uncoated) and the ageing solutions have been characterized, in order to quantify the protective efficiency of the coatings and their ability to limit metal release during exposure. Specific toxicity tests addressed the compliance of coatings with European health and safety regulations. After validation at the bench scale, the feasibility of the best coatings at the upscale level was assessed by industrial partners. The main results concerning the behaviour of the best performing coatings obtained by the B-IMPACT project will be presented.

Synthetic pigments, binder and light: a multitechnique study on degradation of contemporary art materials

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The characterization of ageing of contemporary synthetic binders constitutes an open field in cultural heritage research: the recent and industrial origin of these materials, the unknown interactions with pigments and additives and the less controlled exposition conditions of contemporary art represent important factors to investigate.
In this perspective, this study, part of a PhD project, is aimed to characterize the UVB degradation of an emulsion acrylic binder through spectroscopic –reflectance, FTIR, 1D and 2D-NMR- and spectrometric –ESI-MS- techniques: this approach provides optical and chemical information on the total variation of polymeric species. The focus is directed to the influence of synthetic organic pigments on the ageing process: as assessed for the traditional inorganic pigments (1), organic pigments can play a role on the surface and bulk degradation of polymeric binders (2) and this can be very important for the differential ageing of pictorial films.

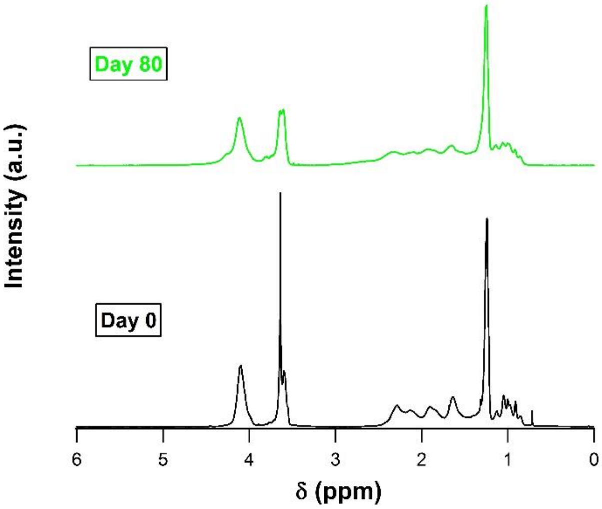

Figure 2: comparison of ^{1}H-NMR binder spectra before and after the ageing process.

The information of this study is related to the ageing of street art samples, whose characterization is gaining a major attention during the last years (3). In fact, street artworks are subjected to aggressive environmental conditions, and the knowledge about their conservation characteristics can result fundamental, even in the perspective of restoration debate about validity of street art conservative operations.

References
1. V. Pintus, M. Schreiner, Characterization and identification of acrylic binding media: influence of UV light on the ageing process, Analytical and Bianalytical Chemistry, 2011, 399, 2961-2976. **2.** Z. E. Papliaka, K. S. Andrikopoulos, E. A. Varella, Study of the stability of a series of synthetic colorants applied with styrene-acrylic copolymer, widely used in contemporary paintings, concerning the effects of accelerated ageing, Journal of Cultural Heritage, 2010, 11, 381-391. **3.** M. M. Di Crescenzo, E. Zendri, M. Sanchez-Pons, L. Fuster-Lòpez, D. J. Yusà-Marco, The use of waterborne paints in contemporary murals: comparing the stability of vinyl, acrylic and styrene-acrylic formulations to outdoor weathering conditions, Polymer Degradation and Stability, 2014, 107, 285-293.

The assessment of the carbonaceous component in black crusts damaging the stone surfaces of historical monuments

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The issue of conservation of the monumental heritage is mainly related to atmospheric pollution that causes the degradation of stone surfaces. Black crusts can be formed as a result of different chemical and physical reactions between the stone surface and environmental factors (such as gaseous pollutants and aerosol particulate matter, PM). These black layers present on the stone monuments reflect the composition of the aerosol particulate matter to which the surfaces are exposed. In particular elemental carbon (EC, also known as black carbon, typically emitted by combustion processes) is the PM component responsible for the characteristic black color of the crusts where it is embedded together with calcium sulphate due to the conversion of calcium carbonate, the main constituent of the stone. Organic carbon (OC) represents the other carbonaceous component of PM and it is present in the black crusts, too. It is of both primary or secondary origin and is linked to numerous sources (traffic, heating plants, biomass burning, etc.).

A deep knowledge of the crust composition in terms of OC and EC optical properties is mandatory in order to get information on the sources responsible for the surface darkening.

OC/EC in PM samples are generally quantified by a reference method (TOT, Thermal Optical Transmittance) not suitable for the analysis of these components in the crusts.

A new approach for OC/EC quantification (1,2) based on a thermal protocol and including CHN and TGA analyses, has been here proposed. The method validation has been performed analyzing suitable reference standard samples prepared by mixing different chemical species in order to simulate the composition of the black crusts present on the monument surfaces.

In addition, the characterization of OC optical properties with UV-visible spectrometry has been performed, to understand the role of light absorbing carbon (i.e. brown carbon) on surface stone darkening. The chemical composition of OC was further investigated with Fourier Transform infrared spectrometry (FT-IR) to identify the contribution of the different organic functional groups to the ageing/browning of stone surfaces.

This research aims to get a new simple method for the evaluation of the carbonaceous component of the black crusts which are formed on carbonate stone surfaces. The protocol has been applied to some real samples of black crusts of different provenance.

References

1. Fermo, P., Turrion, R.G., Rosa, M., Omegna, A., A new approach to assess the chemical composition of powder deposits damaging the stone surfaces of historical monuments, (2015) Environmental Science and Pollution Research, 22 (8), pp. 6262-6270; **2.** La Russa, M.F., Fermo, P., Comite, V., Belfiore, C.M., Barca, D., Cerioni, A., De Santis, M., Barbagallo, L.F., Ricca, M., Ruffolo, S.A., The Oceanus statue of the Fontana di Trevi (Rome): The analysis of black crust as a tool to investigate the urban air pollution and its impact on the stone degradation (2017) Science of the Total Environment, 593-594, pp. 297-309.

A comprehensive study of the effects induced by brown rot fungi on archaeological waterlogged wood

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The archaeological site of Biskupin (Poland) is a prehistoric settlement dating to the 8th century BC, situated on a marshy island. Excavations started in 1934 and a considerable amount of wooden artifacts was found sunken in the water of the lake. Unfortunately, during many years of archaeological excavations, wooden remains deposited in the trenches were exposed to degradation process and underwent decomposition. Among the main causes of wood degradation, fungi and bacteria were the most destructive ones.

The chemical effects induced by fungi and bacteria on wood are not well known or studied. For this reason, we present here a study of a set of wood samples (Pinus sylvestris) buried in the Biskupin site, reproducing the burial conditions of the original archaeological wood. The samples were then removed from the burial environment after 4, 6, 8 and 10 years of deposition in two monitoring stations (wet peat and lake water). After removal from the burial, the samples were exposed to laboratory controlled attack by a brown rot fungus Coniophora puteana. The final aim was to evaluate the effects of fungal activity on the wood substrates with different degrees of natural degradation. The study is part of an experimentation designed to evaluate the short-time effects of the in situ conservation strategy adopted for the Biskupin archaeological woods.

Various techniques were used to assess the physical and chemical degradation of the wood. Physical properties, such as moisture content and conventional density were determined on the basis of the mass of absolutely-dry wood and the volume of the sample in the state of maximal saturation. An attempt to distinguish between the morphological changes induced by the fungal attack and by the exposure to the burial environment itself was carried out through scanning electron microscopy (SEM) examination of the transverse, radial longitudinal and tangential longitudinal sections of the samples The chemical state of preservation was evaluated by using infrared spectroscopy (FTIR) and analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) with in situ silylation. All the results were compared with those obtained for reference materials, including sound pine wood and contemporary and archaeological pine wood attacked by Coniophora puteana.

Carbon Isotope Ratio in Carbonates and Bicarbonates determined by ^{13}C NMR Spectroscopy

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This study focused on the innovative use of ^{13}C NMR spectroscopy for the bulk carbon isotope ratio determination, at the natural abundance, of inorganic carbonates and bicarbonates. Isotope Ratio Mass Spectrometry (IRMS) represents the method of choice for analyses at the natural abundance due to the relative high accuracy (0.1‰) and sensitivity (up to 0.01‰).

However several analytical methods, alternative to IRMS, have been designed and applied for the δ^{13}C analysis, such as mid-infrared laser spectroscopy, non-dispersive infrared spectrometry (NDIRS) and Fourier Transform infrared spectrometry (FT-IR), which offer the advantage of being less expensive and complex.(1)(2)

In the past, NMR spectroscopy has been mainly used to measure the ^{13}C position-specific isotope ratio monitoring (irm-^{13}C NMR) of organic molecules with high precision. The first part of the present study was dedicated to the optimization of spectral parameters for the ^{13}C NMR analysis, necessary to enhance the precision and accuracy on δ^{13}C determinations. Indeed, it was analyzed the influence of relaxation time (T_1), the presence of relaxation agent, the pulse intervals (D_1) and the use of an internal standard on the determination of the δ^{13}C of several carbonates and bicarbonates, comparing the results with those previously determined by means of IRMS.

The determination of ^{13}C/^{12}C ratio of carbonates and bicarbonates (≈50-100 mg) was performed with a precision of the order of 1 ‰ in the presence of a relaxation agent such as $Cr(acac)_3$ and $CH_3{}^{13}COONa$ as internal standard. The sample was prepared by dissolving $CH_3{}^{13}CO_2Na$, sample and $Cr(acac)_3$ in D_2O. Isotope carbon composition of bulk sample was evaluated using linear calibration that is obtained out using two carbonates (Cs_2CO_3 and K_2CO_3) and two bicarbonates ($NaHCO_3$ and NH_5CO_3) with a correlation coefficient r^2=0.9987. The method was applied to water soluble inorganic carbonates and bicarbonates and then extended to insoluble carbonates by converting them to Na_2CO_3 following a simple procedure, without observing isotopic fractionation. By this way the ^{13}C NMR spectroscopy can be also successfully applied for the characterization of the ^{13}C/^{12}C ratio in several different fields such as cultural heritage and geological studies.

References

1. Pironti C.; Proto A.; Camin F.; Cucciniello R.; Zarrella I.; Motta O., *Talanta* 2016, *160,* 276-281; **2.** (a) Zanasi, R.; Alfano, D.; Scarabino, C.; Motta, O.; Viglione, R.G.; Proto, A., *Anal. Chem.* 2006, *78,* 3080-3083. (b) Esler, M.B.; Griffith, D.W.T.; Wilson, S.R.; Steele, L.P., *Anal. Chem.* 2000, *72,* 216-221; **3.** Bayle, K.; Grand, M.; Chaintreau, A.; Robins, R. J.; Fieber, W.; Sommer, H.; Akoka, S.; Remaud, G. S., *Anal. Chem.* 2015,*87,*7550-7554.

Characterization and study of the behaviour of acrylic paint films subjected to artificial ageing: the case of *Edelwachs* acrylic emulsion

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The aim of the present work is to study and evaluate the stability of Pigrol *Edelwachs*® (*Tikkurila GmbH*, Germany). This product, sold as an aqueous emulsion of acrylic copolymers and wax, is generally used as wood protective, but the iconographer Fabio Nones (Trento-1961) has been experimenting its use as an innovative medium for painting. Widely used by Nones and his students, *Edelwachs* has never been studied neither from a compositional point of view nor regarding its stability over time. Its composition was studied by chromatographic (Py-GC / MS) and spectroscopic (FTIR-ATR) techniques that have been commonly applied to characterize acrylic and waxy products (1-3). Based on the results obtained, a combination of methacrylate (MA), methylmethacrylate (MMA), nbutylacrylate (nBA), nbutylmethacrylate (nBMA) monomers was detected, while the waxy component appears to have a microcrystalline nature. Mock-up paints, according to Nones' technique, were prepared by dispersing in *Edelwachs* five inorganic pigments previously characterized using the FTIR-ATR and XRF techniques. The stability to sedimentation of the pure product and of the obtained paints was evaluated by analytical centrifugation tests: the results highlighted that *Edelwachs* is a stable emulsion. To study the stability of *Edelwachs'* films, the mock-ups were subjected to accelerated ageing by photo-catalytic treatments (UV-A and UV-B mix), treatments at low (5-6 °C) and high temperatures (50-100 °C) and exposure to high relative humidity values (HR 85%). As reported in literature (4-6), it is known that these ageing conditions could be potentially critical for acrylates. The effects of the artificial ageing were monitored over time by optical microscopy techniques, colorimetric and VIS-reflectance spectrometry, FTIR-ATR analysis, contact angle measurements and weight variations. The paints show a good stability for all treatments considered, especially those containing titanium white. Thanks to TG-DSC analysis, the main exothermic/endothermic processes and the glass transition temperature (Tg) of the different paints were evaluated before and after ageing: it was observed that the ageing conditions applied may have different effects on the paints depending on the nature of the pigment and the pigment/binding ratio. Moreover, a multi-analytical characterisation of real samples taken from Nones' artworks was carried out. The works, painted out between 2001 and 2016, allowed us to evaluate the characteristics of the naturally aged paints. The morphology of the real samples was observed through optical and electronic microscopy. The composition was studied using FTIR-ATR and SEM-EDS techniques.

References

1. Musser J.B., Kilpatrick P.K., *Molecular Characterization of Wax Isolated from a Variety of Crude Oils*, "Evergy and Fuels", 1998, n°1, pag. 715-725; **2.** Palou A., Cruz J., Blanco M., Larraz R., Frontela J., Bengoechea C. M, González J. M., Alcalà M., *Characterization of the Composition of Paraffin Waxes on Industrial Applications*, "Energy and Fuels", 2014, n°28, pag 956-963; **3.** Pintus V., Wei S., Schreiner M., *Accelerated UV ageing studies of acrylic, alkyd, and polyvinyl acetate paints: Influence of inorganic pigments*, "Microchemical Journal", n°124, 2016, pag. 949-961; **4.** Chiantore O., Lazzari M., *Photo-oxidative stability of paraloid acrylic protective polymers*, "Polymer", n° 42, 2001, pag. 17–27; **5.** Lazzari M., Chiantore O., *Thermal-ageing of paraloid acrylic protective polymers*, "Polymer", n° 41, 2000, pag. 6447–6455; **6.** Domenech-Carbò M. T., Silva M. F., Aura-Castro E. et alii, *Study of behaviour on simulated daylight ageing of artists' acrylic and poly (vinyl acetate) paint films*, "Analytical and Bioanalytical Chemistry", n°399, 2011, pag. 2921-2937.

Multianalytical study for the restoration of a gypsum sculpture of Galleria d'Arte Moderna (GAM) of Milan

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Diagnostic and monitoring are crucial steps in the field of cultural heritage preservation. In particular, diagnostic is usually aimed at characterizing materials and at assessing the state of conservation and degradation processes that affect the artworks.

Given the complexity and heterogeneity of the constituent materials, as well as the possible presence of restoration materials from previous interventions, a multi-analytical approach is generally followed, as it can provide more complete results. In addition, the close collaboration between restorers and conservation scientists is always highly desirable in order to tackle efficiently the conservation issues.

In the occasion of the exhibition "*100 Anni. Scultura a Milano 1815-1915*" at the Galleria d'Arte Moderna (GAM) of Milan, an extensive diagnostic campaign has been conducted on selected artworks prior to their display.

A multi-analytical and micro-invasive approach has been adopted. Preliminary observations, documentation and characterisation of the surfaces has been performed on site by non-invasive techniques. Diagnostic on micro-samples was then performed to precisely characterize the materials, the stratigraphic structure, and to investigate specific deterioration patterns.

Morphological and colorimetric analysis were carried out by means of digital optical microscopy and of spectrophotometric analysis in visible light (colorimetry), both performed *in situ* in a totally non-invasive way. Laboratory analysis on micro-samples were carried out by means of Fourier Transform infrared spectroscopy (FTIR), Raman spectroscopy and scanning electron microscopy coupled with EDX (SEM-EDX) on fragments and polished cross-sections.

The present work is focused, in particular, on the study of the gypsum statue "La Maddalena" by Pompeo Marchesi, which presented a peculiar deterioration pattern. The results of the diagnostic activity clarified the nature and extent of the degradation. Moreover, through the analysis of the stratigraphy, the residual presence of altered finishings due to past restoration interventions was identified. By following an integrated and collaborative approach, the information gathered during the diagnostic activity supported the selection and setup of the conservation methodologies of the restorers for the treatment of the artwork.

Fully biodegradable novel bio-based organogels for the cleaning of artworks

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The cleaning of paintings, which is generally devoted to the removal of aged varnishes, still represents one of the most delicate and potentially hazardous interventions for the safety of operators and the treated surface. Indeed, the most common approach is based on the use of volatile organic solvents applied by cotton swabs. However, this cleaning method has several drawbacks such as the fact that wet procedures do not preserve the health of the restorers and generate wastes. In addition, the solvent may diffuse into the porosity of the underneath layers causing phenomena like swelling and leaching that leave the paint surface brittle with loss of mechanical strength.

In the last years, even if an increased attention has been devoted to the proposal of more healthy products to guarantee the safeguard of the operators, few attentions has been devoted to the development of green methods, which foresee the use of renewable and biodegradable materials.

On these bases, the present research work was aimed at developing fully green novel bio-based organogels for the cleaning of artworks. In particular, different gel formulations were proposed for the cleaning of paintings and of metal surfaces.

The gels were based on poly-3-hydroxybutyrate (PHB) as gelling agent and the formulation were varied with the use of different green solvents.

γ-valerolactone (GVL), ethyl lattate (EL) and dimethyl carbonate (DMC) were selected as active agents in the removal of varnishes from oil paintings and water sensitive paint layers, such as tempera. In particular, the tested gels are completely water free so that they can remove surface varnishes applied on hydrophilic paint layers without affecting them.

Recently, new green gels were also formulated to remove protective organic coatings applied during past restoration on bronze objects. In these cases, the use of less polar solvents (methyl levulinate (ML) allowed the cleaning of aged complex mixtures containing oils and natural and synthetic waxes.

An ad hoc analytical protocol was set up for the evaluation of the performances of the new methods in comparison with the traditional ones.

The gels were tested on painting mock-ups and then validated on real artworks. Encouraging results were obtained on exceptional case studies, such as on the Cimabue masterpiece *The Majesty of Santa Maria dei Servi"* (XIII) located at the Chiesa Santa Maria dei Servi in Bologna (Italy) and on the bronze pulpit (XV) attributed to Donatello and located at San Lorenzo church in Florence (Italy).

Particulate matter and material decay: analysis of dry deposition on horizontal and vertical surfaces exposed through the "Deposition Box" system

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Airborne Particulate Matter (PM), after its removal from the atmosphere through wet and dry mechanisms, can physically/chemically interact with materials and induce premature decay.

In this contest, the effect of dry depositions is a really complex issue, especially for outdoor materials, because of the difficulties related to the collection of atmospheric deposits repeatable in terms of mass and homogeneously distributed on the entire investigated substrate.

To overcome these problems, a new sampling system, the "Deposition Box", was designed, built and validated. The sampler consists of a 50x50x20 cm box, covered by a pitched roof which eliminates the variability induced by removal mechanisms (i.e. winds and rainfalls) in classical outdoor expositions; on the bottom of the box, a fan standardizes the air exchange rate (30 h^{-1}) across the box, ensuring a continuous sampling of ambient air and quite calm conditions inside the box and allowing the deposition to occur.

In the present work, four surrogate materials (Aluminium, Regenerated Cellulose, Cellulose Nitrate and Acetate) with different porosities and surface features were exposed in the urban-marine site of Rimini (Italy). Two mechanisms of PM deposition were differentiated and investigated by analyzing samples exposed both in horizontal (diffusion + gravitational mechanism) and in vertical (diffusion mechanism) positions. Colourimetric measurements were performed on surrogate materials before and after the exposure to quantify the surface soiling due to PM deposition. Beside the mass, the water-soluble fraction of PM has been also characterized by Ion Chromatography (IC) and Atomic Absorption Spectroscopy (AAS). Morphological and dimensional characterization were also performed on particles collected on rounded sheets of adhesive tape mounted on SEM stubs (sampling area: 1.13 cm^2) and exposed both in horizontal and vertical positions.

The promising outcomes suggest that "Deposition Box" can represent an affordable tool to study different PM deposition fluxes and mechanisms on materials and a useful collecting device for the preparation of surfaces for further analyses, aimed at deepening the topic of building and heritage materials decay.

Fig.1: The inner and the external features of Deposition Box during the exposures of surrogate surfaces.

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A new MA-XRF system and an advanced methodological approach for the elemental characterization of panted surfaces: the exceptional case study of the Cimabue's masterpiece

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Chemical maps related to the distribution of elements within a painted surface may provide important information both on the characterization of painting materials and on the definition of proper conservation actions. Indeed, in the recent years, an increasing interest has been devoted to the development of compact macro-XRF systems, establishing the technique as one of the most powerful non-invasive method for the characterization of artworks. In addition, MA-XRF scanners allow the investigation of large painted surface and a reliable documentation with a reduced acquisition time and costs.

However, the big dimension of the data matrix obtained may hamper the correct evaluation of the results. Thus, specific methodological strategies should be defined and followed to collect and extract all the useful information embedded into hyperspectral cubes.

To this aim, the present research work was focused on the evaluation of an advanced, last-generation MA-XRF system: the CRONO scanner developed by XGLab SRL. The instrument is composed of a main XRF unit and of a motorized stage system to implement the scanning. The excitation source is a Rh tube with adjustable maximum voltage (up to 50kV). The X-ray excitation light is collimated to 0.5, 1 or 2 mm, software selectable and a 50 mm^2 Silicon Drift Detector. The speed modulation permits to scan the investigated surfaces varying acquisition time, spatial resolution and spectral quality (S/N ratio), according to type of information required.

The experimental workflow proposed has been applied on an exceptional case of study: the "Madonna Enthroned with the Child and Two Angels" by Cimabue (1240 – 1302), disclosing new reliable knowledges on the masterpiece. The XRF acquisitions allowed a detailed visualization of elements ascribable to pigments used by the artist and a precise localization of several retouched areas. Moreover, a particular attention was addressed to the characterization of the throne decorations. Indeed, elements, such as Cu, Pb, As, Au and Ag were identified, suggesting the use of different execution techniques and pointed out new questions on the originality of some decorative paint effects.

The challenge of orchil dyes:
advanced analytical techniques to discriminate the different lichen species

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Orchil can be considered one of the most intriguing dyes, known during the history of art.

Puh or *phukh* was the name, given by Akkadians and Hebrews, to a purple dye obtained by a "plant", probably the lichen (1). Cited also in *Naturalis Historia* by Pliny for its wonderful violet color, it was also described as "more beautiful than purple from shellfish" by Theophrastus (1). This detail is particularly important, because the prosperity of orchil is almost referable to its property of miming shellfish purple (1). Some sources refer that orchil production was lost in the Mediterranean Sea at the end of Roman Empire and was rediscovered only at the end of Middle Age, thanks to a Florentine merchant, Federigo Rucellai, who, by chance, observed the preparation of violet purple color from the lichen, in the Levant (1). Described in different historical texts during the centuries, its use is well attested until the synthesis of first synthetic dye: the mauveine, which can be considered its synthetic alter ego. The commercialization of this dye has led to disuse of orcein dye.

However, even if the great numbers of citations in the historical texts should bring to many evidences in historical textiles, few research papers are able to demonstrate the presence of orchil dye. The main cause of difficulty in finding orchil dyes is its very high photo-instability (2). This induced a rapid degradation and only few residual molecules of orchil can be observed in textiles manufactures.

In the last years, scientific investigations have been conducted, focusing on optimization of non-invasive (such as UV-Vis fluorimetry) and micro-invasive (such as SERS on fiber) techniques and of proper analytical conditions in HPLC-MS to confirm the presence of phenoxazone compounds (2-5). Furthermore, under the name of orchil several species of lichens, not only *Roccella tinctoria* DC. (one of the most famous) can be counted: at least 60-70 species of lichen are able to produce phenoxazone compounds after a treatment in ammonia.

Taking into account these evidences, the present work is focused on a multi-analytical approach, as a powerful tool to develop a secure protocol for the detection of orchil dye. Furthermore, it would investigate the possibility of discriminating among the different species of lichens, such as *Roccella tinctoria* DC., *Lasallia pustulata* L., *Ochrolechia tartarea* L.

Starting from SERS on fiber analyses, on the yarns dyed with the different lichen species, the research has been conducted applying a new extraction protocol from dyed yarns (6) and the residue obtained has been used for a separation through HPTLC. Then, HPTLC-SERS spectra have been acquired for each spot on TLC plates and this information has been got together with those obtained from HPTLC-MS experiments. This would led to the identification of main phenoxazone compounds, in charge of the colour, but also secondary compounds which, probably, could be identify as markers, useful to distinguish among the several lichen species.

References

1. D. Cardon, Le Monde des Teintures Naturelles, Edition Bèlin, Paris, 2014; **2.** F. Rosi F., C. Clementi, M. Paolantoni, A. Romani, R. Pellegrino, B. G. Brunetti, W. Nowik, C. Miliani, Journal of Raman Spectroscopy, 44 (10), 2013, 1451-1453; **3.** C. Clementi, C. Miliani, A. Romani, G. Favaro, Spectrochimica Acta Part A 64, 2006, 906–912;
4. M. Aceto, A. Arrais, F. Marsano, A. Agostino, G. Fenoglio, A. Idone, M. Gulmini, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 142, 2015, 159-168; **5.** B. Doherty, F. Gabrieli, C. Clementi, D. Cardon, A. Sgamellotti, B. Brunetti, C. Miliani, Journal of Raman Spectroscopy 45 (9), 2014, 723-729; **6.** L. Lombardi, I. Serafini, M. Guiso, F. Sciubba, A. Bianco, Microchemical Journal 126, 2016, 373–380.

Life Cycle Analysis of a pyrolysis process applied to end-of-life tires

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The "Sustainability Report 2015" of Ecopneus states that the total collection of end of life tires (ELT) in 2015 amounted to 247966 tons and of these 246128 tons were managed through mechanical and thermal treatments because ELT represents both an important resource of materials (especially rubber, 40% in weight, and steel) and of energy. For this purpose, the goal of the work has been the assessment of the environmental impacts of a novel pyrolysis process of ELT, designed by the company Curti s.p.a. and the comparison with alternative valorization and/or disposal scenarios. It is important to outline that Curti plant is different from the other already on the market because it only needs a simple pre-treatment step (1) for ELT.

Life Cycle Analysis methodology (LCA) has been so applied to determine the most critical stages of the process under study, assessing the environmental benefits arising from the recovery of materials and energy and the greater or lower impact compared to the mechanical or thermal technologies already on the market, choosing the boundaries of the system "from gate to gate", taking into account treatment processes, materials recovery and disposal of waste water\residues, and as functional unit (FU) 1 ton of ELT treated by the Curti plant.

First, a comparison between different pretreatment scenarios performed in other recovery processes, has been performed, taking into account: single cut, grinding, crushing and pulverization. After, the whole environmental impact of the pyrolysis plant managed by the company Curti s.p.a. has been analysed. Then, pyrolysis process has been compared to other scenarios of recovery of energy: the management of 1 ton (FU) of ELT has been compared also for cement plant and waste to energy process (2). Lastly, the comparison of different scenarios of material recovery with the pyrolysis process has been realized. The different scenarios realized have been analyzed through three different method of analysis: first using the ReCiPe analysis method, considering five impact categories at midpoint level: climate change, human toxicity, particulate matter formation, fossil fuels depletion and metal depletion; three categories of damage were also considered: human health, ecosystem quality and resources depletion. Then, the environmental assessment step has been completed using also the Cumulative Energy Demand (CED) and the Global Warming Potential (GWP) methods, to investigate potential impacts in terms of energy demand and of CO_2 equivalent emission. Considering only the pre-treatments, the pyrolysis process has an environmental impacts equal to 1/3, 1/10 and 1/20 compared with grinding, crushing and pulverization, especially in terms of climate change and fossil depletion. The analysis of Curti pyrolysis process showed that the avoided impact due to the recovery of carbon black, steel and oil fuel exceeds widely the impact generated by the process. Compared to other energy-recovery scenarios, a greater advantage results for the pyrolysis process. Then, comparing it to other materials recovery scenarios, a huge influence is given by the different options of recovery considering which materials actually they replace, considering a full recovery of metals and rubber (to replace the synthetic rubber) or intermediate options: this second scenario would bring to a greater gain from the environmental point of view for the Curti pyrolysis technology.

References
1. Giorgini L. et al., 2015, "Efficient recovery of non-shredded tires via pyrolysis in an innovative pilot plant", EEMJ, 14, 1611-1622. **2.** Passarini, F. et al., 2014. "Environmental impact assessment of a WtE plant after structural upgrade measures", Waste Management.

LCA methodology: a case study of the industrial production of terephthalic acid from renewable sources

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The scope of the present study is to investigate the environmental sustainability of different routes of terephthalic acid (TA) production from renewable sources in order to identify which of the selected pathways has the lowest environmental load. The comparison was performed between five different production processes: GEVO® (1), BioForming® (2), TA from DMF and acrolein (3), TA from HMF and ethylene (4), and an alternative pathway from p-cymene (5). The first two are already set at industrial level, while the others are still under development. All scenarios needed to build the synthesis routes were therefore modeled in order to obtain, starting from biomass, the production of terephthalic acid. Among those investigated, four ways provide for the formation of p-xylene, subsequently oxidized to terephthalic acid through the Amoco® process, while the last is proposed as an alternative because it uses p-cymene as a precursor to obtain the molecule of interest. In order to do it the methodology LCA (Life Cycle Assessment) has been used as a scientific tool of analysis and evaluation of the potential impacts of each scenario. LCA is a method of analysis which allows the evaluation of the environmental weights associated with the entire life cycle of a product or a process, through the identification and quantification of energy and material flows in input and in output from the system under consideration. LCA studies may consider all aspects related to the life cycle of the system using an approach "from cradle to grave" or limited (as in this case) to its production phase ("from cradle to gate"), imagining a uniformity of the destiny (use and disposal) for the downstream stages. The potential impacts are evaluated by comparison with CED method (Cumulative Energy Demand), that analyze the needs of direct and indirect resources expressing the result in energetic terms, and ReCiPe method, which divide the environmental loads in intermediate categories of impact (midpoint level), that can be grouped into categories of damage to the receptor (endpoint level). The results of the analysis show that for all scenarios the principally responsible categories for the impacts are those that are directly related to the production and cultivation of the starting biomasses. The main category associated with the major contribution is the *Agricultural land occupation*. This tendency is connected to the bio-based nature of the processes, therefore we also included in the assessment the following categories: *Natural land transformation*, *Freshwater eutrophication*, *Terrestrial acidification* and *ecotoxicity*, but these show more marginal responsibilities. Among the investigated scenarios the process from DMF and acrolein is the one that presents the worst results in environmental terms for all the comparisons made, while the alternative pathway from p-cymene turns out to be the most promising. The reason of this result is due to the fact that we consider a waste biomass for the production of p-cymene (orange peels), instead a dedicated culture as for the other scenarios.

References
1. United States patent US 9217114B2, 2015; **2.** United States patent US 2011/0087000A1, 2011; **3.** Chem. Eur. J. 2011, 17, 12452–12457; **4.** Ind. Eng. Chem. Res. 2014, 53, 10688−10699; **5.** ChemSusChem. 2016, 9, 3012-3112.

Application of an electro-activated glassy carbon electrode (GCE) to the analytical monitoring and photochemical studying of acetaminophen

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The occurrence of emerging contaminants in surface waters, such as pharmaceuticals and personal-care products, is an environmental issue of high concern due to the toxic effects on ecosystems and humans (1). *Waste Water Treatment Plants* (WWTPs) are usually not able to remove these compounds from wastewater because they are water soluble and biorefractory. Therefore, emerging contaminants are often released in water bodies. As far as pharmaceuticals are concerned, antibiotics, analgesics and anticonvulsionants are usually detected in surface waters (2). In these environments, xenobiotics can undergo both abiotic and biotic degradation. Among abiotic pathways, direct and indirect photochemical reactions can be key degradation processes. Direct photolysis occurs when the xenobiotic absorbs the solar light and undergoes subsequent chemical transformations. In contrast, indirect photolysis is triggered by *Photochemically Produced Reactive Intermediates* (PPRIs) that react with xenobiotics. The main PPRIs are $HO^{\bullet}$, $CO_3^{\bullet-}$, excited triplet states of Chromophoric Dissolved Organic Matter ($^3CDOM^*$) and $^1O_2$. They are formed upon absorption of solar light by photosensitizing compounds, such as CDOM, nitrate and nitrite (3). Usually, photochemical reactions act as self-depuration processes in water bodies, but they can also induce formation of harmful photodegradation products. Luckily, the photochemical fate of xenobiotics (half-life times and photoproduction of intermediates) can be modeled, and thus foreseen, by knowing or measuring the relevant photoreactivity parameters (e.g., reactions rate constants and photoproducts formation yields) and by using suitable photochemical models (4). Therefore, the monitoring of xenobiotics concentration in both WWTPs influents/effluents and surface waters, and the understanding of the photochemical fate of these compounds, are important tools to assess the human impact on aquatic environments.

Acetaminophen (also known as paracetamol, hereafter APAP) is a widely used analgesic drug usually detected in surface waters (2) at concentrations up to 10 μg L^{-1} (5). In this work, we have focused on the use of *Differential Pulse Voltammetry* (DPV), with a recently implemented electrochemically activated glassy carbon electrode (aGCE) (6), for the monitoring of APAP in the surface waters of the Po river basin, in the province of Turin (Piedmont, Italy). In order to confirm the reliability of the electrochemical response, we have compared DPV results with those obtained with *High Performance Liquid Chromatography* hyphenated with *High Resolution Mass Spectrometry* (HPLC-HRMS), commonly used to quantify pharmaceuticals. Furthermore, DPV with the aGCE was used to assess the photochemical degradation of APAP, and the relevant kinetic results were compared to those obtained in a previous work with a standard experimental methodology (7). The purpose is to make it possible to monitor the APAP photodegradation, and the formation of photoproducts, in real-time by developing an adequate electrochemical set-up.

References

1. Schwarzenbach et al., Science, 2006, 313, 1072. **2.** Stamatis and Konstantinou, J Environ Sci Heal B, 2013, 48, 800. **3.** Vione et al., Chem. Eur. J. 2014, 20, 10590. **4.** Bodrato and Vione, Environ. Sci.: Processes Impacts 2014, 16, 732. **5.** Heberer et al., Toxicol. Lett. 2002, 131,5. **6.** Chiavazza et al., Electrochim Acta, 2016, 192, 139. 7. De Laurentiis et al., Water Res., 2014, 53, 235.

Removal and photodegradation of glyphosate herbicide from waters using a mesoporous substrate with adsorbent properties

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Nowadays, a large amount of pesticides is used worldwide and many of these substances penetrate the soils, polluting water resources. Among these compounds, glyphosate is a non-selective herbicide recently classified as a probable carcinogen for humans (Group 2A). Conventional water treatment techniques are not effective in its removal, therefore the scientific community is exploring new approaches for the removal of glyphosate from aquatic systems.

In this work, we evaluate the adsorption and degradation properties towards glyphosate of a mesoporous silica-based support, encapsulated with iron oxides and functionalized with (3-aminopropyl)triethoxysilane (SBA-15-FexOy-NH_2). Results demonstrate the excellent adsorption performance of the SBA-15-FexOy-NH_2 towards glyphosate. Indeed, the adsorption is very fast and reaches equilibrium during the first 10 minutes of contact. Through the adsorption isotherms, the maximum monolayer coverage capacity (98 mg/g) was obtained. The adsorption properties of SBA-15-FexOy-NH_2 were also studied in the presence of high concentration of PO_4^{3-} (40 mg/L), a potential competing ion frequently present in water resources. Results indicate that the material keeps unaltered its adsorption performance, while at the same time removing PO_4^{3-} from the aqueous solution.

The presence of Fe in the substrate was intended to trigger photodegradation reactions; in particular, photo-Fenton reactions were studied at pH 3.0 and 6.5 under UVA and UVB irradiation. The most effective method was UVB irradiation at pH 6.5; these conditions allowed the successfully degradation (90%) of the previously adsorbed glyphosate. Worth noting it was observed the retention of the glyphosate by-products on the SBA-15-FexOy-NH_2 sorbent, thereby preventing the release of additional molecules into the aqueous matrix. It was shown that the photo-Fenton treatment regenerates the material and makes it possible to carry out at least three adsorption-degradation consecutive cycles, without any loss in performance.

Finally, the adsorption and photodegradation capabilities of the material have also been verified on a Po river water sample, thus showing the possible application of the sorbent even in matrices that are affected by high amounts of possible interfering species (e.g. organic matter).

The study here presented is part of a PhD research program.

Characterization of ionic composition in the submicron fraction of urban aerosol

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Atmospheric particles are polydisperse, varying the diameter of more than four orders of magnitude: from some nanometers (nm) to tens or hundreds of micrometers (µm) (1). Particle size is one of the most important parameters to monitor particles' behavior in the atmosphere because it indicates the type of source and influences transport and deposition processes. Particle size distribution and concentrations of ionic species are quantified to determine their potential sources of input, chemical evolution and transport (2).

The main aim of the present work was to investigate the particle size distribution of ionic compounds (Cl^-, Br^-, I^-, NO^{3-}, MSA, SO_4^{2-}, PO_4^{3-}, C_2-oxalic acid, C_2-glycolic acid, C_2-acetic acid, C_3-malonic acid, cis-usC_4-maleic, trans-usC_4-fumaric, C_4-succinic acid, αC_7-benzoic acid, C_5-glutaric acid, hC_4-malic acid, C_6-adipic acid, C_7-pimelic acid, Na^+, NH_4^+, K^+ and Mg^+) in urban aerosol collected at Venice. We used 120 MOUDI^{TM} II sampler that permitted to separate particles in 12 dimensional fractions starting with a diameter greater or equal to 18 µm to a diameter below of 56 nm. The sampling was carried out during the 2016 spring season between March and May.

The determination of anionic compounds was performed using ion-chromatography coupled to mass spectrometry (IC-MS), while cationic species were determined through capillary ion chromatography with conductometry (2).

The concentration of ionic compounds in the aerosol samples represented the highest percentage of aerosol mass concentration. The study of the ionic composition and their particle size distribution in the analyzed samples has allowed to identify different sources, as well as marine input and anthropogenic contribution.

References:

1. P. H. Mcmurry, "A review of atmospheric aerosol measurements ઙ," vol. 34, 2000.
2. E. Barbaro et al., "Particle size distribution of inorganic and organic ions in coastal and inland Antarctic aerosol," pp. 2724–2733, 2017.

Sea salt sodium record from Talos Dome (East Antarctica) as a potential proxy of the Antarctic past sea ice extent

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Sea-ice represents a powerful phenomenon exerting a strong influence on the oceanic, biological and climatic systems and, given its importance, it is a focus in environmental research. The expansion and retreat of Antarctic sea-ice is one of the most striking seasonal changes affecting the Earth today, effectively increasing by two fold the surface area of Antarctica. Despite an unknown exact mechanism, sea-ice plays a critical role in the polar amplification of climate change and, therefore, it is important to predict changes in sea ice under the future conditions of an ongoing climate change. A better understanding of the links between sea-ice and climate and a real improvement of the models requires a large series of long observational datasets. Antarctic sea ice has shown an increasing trend in recent decades, but with strong regional differences from one sector to another of the Southern Ocean. The Ross Sea and the Indian sectors have seen an increase in sea ice during the satellite era (1979 onwards). Here we present a record of $ssNa^+$ flux in the Talos Dome region during a 25-year period spanning from 1979 to 2003, showing that this marker could be used as a potential proxy for reconstructing the sea ice extent in the Ross Sea and Western Pacific Ocean at least for recent decades. After finding a positive relationship between the maxima in sea ice extent for a 25-year period, we used this relationship in the TALDICE record in order to reconstruct the sea ice conditions over the 20th century. Our tentative reconstruction highlighted a decline in the sea ice extent (SIE) starting in the 1950s and pointed out a higher variability of SIE starting from the 1960s and that the largest sea ice extents of the last century occurred during the 1990s. Our findings were also compared to other ice core reconstructions of Antarctic past sea-ice extent.

A six-year record of size distribution and chemical composition of Arctic aerosol. Main results and future bi-polar perspetives.

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The Arctic regions are among the areas most sensitive to present climate changes; through connections involving ocean, atmosphere, biosphere, lithosphere and cryosphere, they respond to, amplify, and drive changes elsewhere in the Earth system, so that understanding their role the climate-environmental feedback processes is essential to set reliable predictive climate models. In particular, the atmospheric aerosol strongly interacts with the climate forcings through scattering and absorption of the solar irradiation and as sources of cloud condensation nuclei. Although these processes are well known, the quantitative and qualitative (the sign of the climate forcing) of the aerosols in the Polar Regions is affected by a large uncertainty, yet. The main uncertainties include the relative cloud/snow surface albedo and the scarce spatial coverage of size distribution and chemical composition of aerosol at high latitudes. To improve our knowledge on the size distribution, the atmospheric load and the chemical composition of the Arctic aerosol, continuous measurements and sampling campaigns are ongoing since 2010 in two Arctic sites: Thule (North Greenland) and Ny Alesund (Svalbard Island, Norway). At Thule, 24-h samples are all-year-round collected at daily or every other day resolution. Contemporaneously, "summer" (March to September) aerosol was annually sampled at Ny Alesund. In the latter site, aerosol was collected by several systems (PM10 samplers, multi-stage impactors (4- and 12-stage Dekati samplers) and on different substrates (Teflon filters, quartz filters, polycarbonate and Teflon membranes). Besides, shorter measurement and sampling campaigns were carried out by using a tethered balloon, up to about 1.000 m altitude, to study the effect of the PBL dynamics on the aerosol atmospheric load and chemical composition. Filter chemical analysis includes: ions composition (inorganic anions and cations and selected organic anions, including light carboxylic acids and MSA), elemental composition (by PIXE analysis), main and trace metals (including Rare Earth Elements - REEs, by ICP-HR-MS), Pb isotopic ratios (by ICP-QMS) and Elemental/Organic Carbon fractions (EC/OC, by Sunset thermo-optical analysis). Besides, continuous measurements of particle size-distribution (TSI-SMPS and TSI-APS; 6 nm – 20um; 10 min resolution), Black Carbon (by Particle Soot Absorption Photometry – PSAP) and natural radioactivity (Rn progeny, by FAI PBL Monitor) were carried out during the sampling periods at Ny Alesund. Here we report the most relevant results up to now obtained and the future perspective both concerning Arctic and Antarctic aerosol, in the framework of three PNRA (Progetto Nazionale di Ricerche in Antartide) projects recently approved and funded. In particular, the use of specific chemical markers (such as nss-sulfate for anthropic Arctic Haze, REEs elements for dust, MSA for biogenic emissions, selected heavy metals for local and long-range anthropic sources) allowed studying the changes in sources intensity and atmospheric transport efficiency for aerosol reaching the Arctic regions. Sulfate source apportionment was performed to evaluate the contribution of sea spray, continental dust, biogenic emissions and anthropic activities to the sulfate global budget. MSA was used to understand the complex interactions among sea ice dynamics, chlorophyll blooms and marine primary productivity. Lead isotopic composition and REEs composition were used in identifying the continental source of dust and anthropic pollutants. Finally, a relationship between marine biogenic emissions and nucleation events was found by particle size distribution in the nanometric mode.

Effects of biomass, temperature and thermochemical process on PAH concentration in biochar

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Biochar is the solid carbonaceous material produced by the pyrolysis of biomass for a variety of applications in the agro/environmental field (1). The thermochemical processes of biomass also produce a variety of organic compounds including PAHs, highly harmful compounds to man and to the environment.

The effects of biomass, temperature and type of process (pyrolysis and gasification) on 16 US EPA PAH concentration in biochar were investigated. To this end, 47 biochars were analyzed for their PAH content. 38 of them were produced in laboratory furnace, in highly controlled pyrolysis conditions, from 11 biomasses of which 7 were of wood (beech, chestnut, pine, poplar, spruce pine, commercial conifer, and pruning from fruit tree and grape vine) and 4 of grass (thistle, giant cane, rice straw and miscanthus leaves). The temperatures of pyrolysis were 350, 550, 750 and 1000 °C. In addition, 6 biochars were produced in industrial plants of pyro-gasification or pyrolysis. These plants were fueled with six of the biomasses used in the laboratory pyrolysis (spruce pine, conifer, pruning, thistle, giant cane and rice straw). Finally, 2 biochars (named STG and SPG), produced in a small experimental plant of gasification, and a biochar commercially available were considered. For the latter the production conditions were not known.

Examining the sum of the concentrations of 16 PAHs (Σ_{16}PAH) of each laboratory biochar, it can state that the type of biomass (wood or grass) does not affect the Σ_{16}PAH, but this Σ_{16}PAH depends on single biomass. Although the highest Σ_{16}PAH values related to the type of biomass were found at 350 °C for wood biochars and 550 °C for grass biochars. The Σ_{16}PAH at the highest temperatures studied (750 and 1000 °C) were always lower than values of the other temperatures. Other interesting considerations that can be made concern single PAHs trapped on biochar at 350, 550 and 750 °C. For instance, all 16 PAHs were present at 550 °C except acenaphthene, and naphthalene and phenanthrene were found to be the most common and abundant PAHs. The process (pyrolysis or gasification) influences on the concentration of PAHs in biochar, however, the design of the reactor used and the working temperature are also important. The fact that the produced gas passes through or not the char bed to exit from reactor is an important factor. The lab. pyrolysis, in which the produced gas is continuously brought away by inert gas, gave biochar with Σ_{16}PAH lower than pyro-gasification, in which the syngas passes through the char bed. For example, Σ_{16}PAH were 455 and 3989 µg/kg for lab. pyrolysis and ind. pyro-gasification biochars, respectively. In this study the ind. pyro-gasification biochars were generally characterized by PAHs that did not include those with MW > 228 uma, unlike the biochar from ind. pyrolysis that contained 15 of the 16 US EPA PAHs. Considering the TEC (toxic equivalent concentration) values, the ind. pyro-gasification biochars investigated are suitable for their potential use as soil amendments.

In conclusion, it can be said that to produce biochar with lower PAH content is necessary choose the suitable parameters concerning the feedstock, temperature, process and design of the reactor.

Reference: 1. M. Ghidotti, D. Fabbri, A. Hornung, Profiles of Volatile Organic Compounds in Biochar: Insights into Process Conditions and Quality Assessment, ACS Sustain. Chem. Eng. 5 (2017) 510–517. doi:10.1021/acssuschemeng.6b01869.

Particulate and gaseous indoor contamination at the Museum of "Last Supper" of Leonardo Da Vinci: results from one year of monitoring activity

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Atmospheric particles and gaseous pollutants can affect cultural heritage, especially the most fragile, such as The Last Supper of Leonardo da Vinci. During the centuries, The Last Supper became a case in establishing the extent of the issue of environmental conditions for the preservation of the Leonardo's masterpiece. The Leonardo's painting is protected by a filtering system (1). Previous indoor studies in the Last Supper museum were aimed to the indoor/outdoor penetration of particulate matter (2). Uncertainties concerning the particles dynamics and the gaseous contamination still persist. At this purpose, a specific experimental setting was developed allowing to perform continuous, high-time resolution, monitoring activity: a novelty in the field of conservation of cultural heritage.

Measurements (March 2016-April 2017; 1 min time res) were conducted using a combination of: 1) Aethalometer (AE-33, Magee Scientific, 7-λ), 2) condensation particle counters (TSI 3787), 3) an optical particle counters (Grimm 1.107), 4) a low volume sampler (Mega system) 5) a custom developed rotating impactor, 6) a real-time NH_3-NO_x-O_3 detector (Environment spa) and 7) passive and active CO_2, samplers were used in order to determine the isotopic ratio $^{13}C/^{12}C$ ($\delta^{13}C$) using a newly developed method (3). A Ca-based sorbent, $CaO/Ca_{12}Al_{14}O_{33}$, 75:25 w/w, was used for passively collecting atmospheric CO_2, and an Ascarite®-based sorbent for the active sampling; the collected CO_2 was desorbed from the substrate with acid treatment and directly analysed by non dispersive infrared spectroscopy (NDIRS).

Whereas particles concentrations reached the low level reported in previous studies (1), the high time resolution showed their diurnal cycle: the total number concentration reached a value of 20.7±0.1 cm^{-3} (BC was 8±1 ng m^{-3}) during night and then increased with visitors up to 167.8±3.3 cm^{-3} (BC was 37±4 ng m^{-3}) during daytime. These values remained however far from outdoor pollution levels (~1-$2{*}10^4$ cm^{-3} and ~1000-2000 ng m^{-3}) highlighting the efficiency of the filtering system. The impact of visitors was also confirmed by CO_2 data that revealed a decreasing $\delta^{13}C$ values with increasing the number of visitors. The results on the isotopic composition of CO_2, correlated to the variation of atmospheric CO_2 concentration, permitted to follow the anthropogenic impact in the different areas of museum and were used such as a non-invasive marker to detect the air circulation and to improve the filtering system operations.

The diurnal cycle of primary and secondary particles was also investigated obtained using the apportionment of particle concentration based on N/BC ratio (4). A secondary particles peak in the afternoon (up to 300 m^{-3}) was observed. Also the NH_3 concentration peaked in the afternoon reaching a double concentration than that observed during night-time.

Moreover, the chemical composition of collected PM samples showed a mass fraction of NH_4NO_3 of 7% inside the museum that, compared with the external value of 30% highlighted the volatilization and decomposition of NH_4NO_3. The presence of ammonia became a driver of new particle formation.

References

1. Gasparini F., Stolfi G., Il Cenacolo Vinciano: impiantistica e microclima all'interno del Refettorio., 2014; **2.** Daher et al., Environ. Sci. Technol., 2011, 45 (24), pp 10344–10353; **3.** R. Cucciniello et al.. Atmospheric Environment 60 (2012) 82-87; **4.** Reche at al., Atmos. Chem. Phys., 11, 6207–6227, 2011.

Comunicazioni Poster

Supporting the development of sustainable nano-based formulations for the restoration of modern and contemporary works of art

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Currently there is a lack of methodologies for the conservation of modern/contemporary artworks, many of which will not be accessible in short time due to extremely fast degradation processes. In this context, the application of nanotechnology already showed promising results and more solutions are currently being explored in the frame of the NANORESTART (NANOmaterials for the REStoration of works of ART) H2020 project. In particular, the project aims at developing nano-based formulations to ensure long term protection and security of modern/contemporary cultural heritage, taking into account environmental and human risks, feasibility and materials costs. Specifically, it focuses on: (i) tools for controlled cleaning, such as highly retentive gels for the confinement of enzymes and nanostructured fluids based on green surfactants; (ii) the strengthening and protection of surfaces by using nanocontainers, nanoparticles and supramolecular systems/assemblies; (iii) nanostructured substrates and sensors for enhanced molecules detection. To support the developers of new materials in designing safer and sustainable products, a four steps strategy was designed and is currently adopted in the project. First, a list of potential ingredients (along with their Material Safety Data Sheets) is collected for each proposed innovative formulation together with its composition (as ranges of percentage in weight for each ingredient). This allows to apply the self-classification approach included in the EU Classification, Labelling and Packaging (CLP) regulation with the aim to classify each formulation according to a set of human health and environmental hazards and to advise the material developers about weight thresholds that should not be exceeded in order to avoid specific hazards. Secondly, information on conventional counterparts already in the market (including their Safety Data Sheets) are collected to prioritize the most promising new formulations: on these products physico-chemical characterization in environmental and biological media as well as (eco)toxicological testing are performed. Toxicity tests are carried on according to internationally standardized testing protocols (ISO and OECD) and EU REACH regulation requirements [e.g. in vitro: SOS-ChromoTest and UMU-ChromoTest; in vivo: MicrotoxTM, microalgae (Pseudokirchneriella subcapita) and Daphnia magna]. Physico-chemical characterization includes spectroscopic and light scattering techniques [Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), analytical centrifuge (Dispersion Analyser) and Dynamic Light Scattering (DLS)]. Estimated toxicity are then compared to the results of the self-classification approach in order to identify possible nano-specific hazards. Results support the third step, when environmental impacts along the life-cycle of the formulations are assessed (in particular in application and post-applications stages). Finally, in the fourth and last step, environmental impact assessment results are combined with technical (e.g. stability, compatibility, re-treatability), economic (e.g. market price) and social (e.g. ethical) criteria in order to derive a conclusion on the overall sustainability of the innovative nano-based products.

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Portable Infrared Spectroscopy for the Non-invasive Analysis of Cultural Heritage Objects

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Infrared spectroscopy has been widely employed for the characterization and study of cultural heritage materials. But most FTIR spectrometer are located in laboratory and the analysis can be performed only on small samples, when a sampling is possible. Several in-situ infrared spectrometers have been used for the investigation of artworks. In this research, the performances of a portable infrared spectrometer will be presented together with some case study and applications. In particular, use of the diffuse reflectance infrared Fourier transform (DRIFT) device will be discussed and our recent results on the development of an infrared library database collection for the non-invasive identification of canvas grounds and colorants will be presented (1). The DRIFT spectroscopy has been also tested for the non-invasive characterization of a watercolor from Graham Vivian Sutherland (2). Moreover, we will show the use of ATR-FTIR spectroscopy for the characterization of the best consolidation treatment for the restoration of the rubber artwork “Presagi di Birnam” from Carol Rama (3). Lastly, a study on the degradation plastic materials used in contemporary art has been carried out performing an artificial accelerated ageing in solar box and the chemical-physical alterations were monitored through the new portable instrument (4).

References

1. Manfredi, M., Barberis, E., Rava, A., Robotti, E., Gosetti, F., Marengo, E., Portable diffuse reflectance infrared Fourier transform (DRIFT) technique for the non- invasive identification of canvas ground: IR spectra reference collection, Analytical Methods, (2015), Vol. 7, Issue 6, Pages 2313-2322; **2.** M. Manfredi, E. Barberis, M. Aceto, E. Marengo, Non-invasive Characterization of Colourants by Portable Diffuse Reflectance Infrared Fourier Transform (DRIFT), Spectrochim Acta A Mol Biomol Spectrosc. 2017 Jun 15;181:171-179; **3.** Manfredi M., Barberis E., Rava A, Poli T, Chiantore O., Marengo E., An analytical approach for the non-invasive selection of consolidants in rubber artworks, Anal Bioanal Chem. 2016 Aug; 408(21):5711-22. doi: 10.1007/s00216-016-9673-y. Epub 2016 Jun 2;

4. Manfredi M., Barberis E, Marengo E., Prediction and Classification of the Degradation State of Plastic Materials Used in Modern and Contemporary Art, Applied Physics A, Volume 123, Issue 1, Article number 35, 2017.

Aspetti giuridici e tecnologici nella valorizzazione dei materiali di scarto

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Gli sforzi verso l'attuazione effettiva del principio dello sviluppo sostenibile in un contesto concorrenziale sempre più ampio ed a più velocità hanno portato in primo piano il tema della potenzialità dei processi di valorizzazione dei materiali di scarto e, più in generale, dell'uso di sostanze alternative alle materie prime tradizionali. I sistemi premiali (anche in termini di competitività) per le produzioni a ridotto impatto ambientale, unitamente alla crescente sensibilità per il c.d. ciclo di vita del prodotto, hanno comportato una crescente sensibilità dei mercati verso settori in cui l'obiettivo della prevenzione della produzione di rifiuti diventa una voce primaria nei *business plan*. Tale processo coinvolge stakeholders con competenze e priorità estremamente diverse, circostanza che, se da un lato comporta la possibilità di creare sinergie estremamente positive, dall'altro a volte rischia di frenare l'attuazione sul piano industriale dei processi innovativi volti alla valorizzazione della materia.

In particolare, l'esigenza di una regolazione comune che l'Europa cerca di soddisfare, unitamente alle specificità nazionali irrinunciabili ed alle peculiarità di ogni singolo progetto, rendono ad oggi la sperimentazione e, soprattutto, lo sfruttamento a livello industriale dei risultati dell'innovazione tecnologica tutt'altro che agevoli. L'esempio dei materiali di scarto è emblematico. Da un lato, infatti, l'obiettivo della riduzione, a monte, della produzione dei rifiuti, comporta la creazione, sul piano spesso prima giuridico che tecnologico, di categorie teoriche di incerta applicazione (si pensi al caso dei sottoprodotti); dall'altro lato, la possibilità di valorizzare i rifiuti mediante processi di recupero innovativi rischia di trovare un freno nei procedimenti autorizzativi finalizzati al controllo preventivo sull'attuazione di tali processi a livello imprenditoriale. I conflitti tra i diversi interessi che vengono in considerazione (ambientali, economici, sanitari, pubblici, collettivi, diffusi …) rischiano, in un contesto tecnologico globale sempre più dinamico, di creare un potente freno allo sviluppo della sinergia tra il mondo dell'industria e quello della ricerca.

Al fine di mostrare concretamente gli effetti di quanto sopra illustrato, verranno presentati alcuni casi studio riguardanti processi di valorizzazione di materiali di scarto la cui fattibilità tecnologica è stata verificata in laboratorio:

i) produzione di materiali da costruzione e di aggregati leggeri con funzione fertilizzante per uso agricolo a partire da materiali di scarto dell'industria agro-alimentare (gusci d'uova, cenere di lolla di riso, sansa d'oliva, semi d'uva, noccioli di frutta, cenere di farina d'animali, tutolo di mais);

ii) produzione di vetri, vetro-ceramici e geopolimeri a partire da materiali di scarto dell'industria inorganica (diverse tipologie di vetro di scarto, come da imballaggio, da lampade fluorescenti e da tubo catodico, scorie d'acciaieria, scorie da inceneritore di rifiuti solidi urbani).

Per ciascuno di questi casi, verrà condotta un'analisi approfondita sulla base della normativa vigente, in modo tale da mettere in luce le eventuali criticità di carattere giuridico-economico che potrebbero ostacolare, se non addirittura impedire, una trasferibilità a livello industriale dei processi in esame.

LCAs of different niche animal based food products: an overview

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Livestock constitutes the 9% of global greenhouse gases (GHG) emission (3057 Mton CO_2eq per year) (1), 54% of which are due to bovine livestock. Information on product supply chains is therefore fundamental to raise awareness of consumers on the environmental implications of their food choices. This study, promoted by the Slow Food Foundation (2), aimed at providing quantitative information on lifecycle of products in order to support their qualitative description. The method Life Cycle Assessment (3,4) (hereafter LCA) was used to estimate the potential environmental impacts (i.e. Carbon Footprint) due to the supply chain of different niche animal based food products: beef and pork meat, cheese and eggs. All the 7 farms under study were characterized by semi-wild breeding, slow growth, autochthonous races and auto-produced animal feed.

The system boundaries take into account the overall lifecycle of each product, from organic feed production to livestock management, product transformation and packaging. Biogenic emissions, due to enteric fermentation and manure management, were also included and evaluated by specific models (5,6).

Results from LCA of these products were very clear and always highlighted lower values than other conventional (industrial) productions (i.e. average value based on data from scientific literature (7). In particular, emissions for beef meat production are about 28% lower than European average values, 16% lower for pork meat, 74% lower for cheese and 37% lower for eggs. These differences are mainly due to the farm management e.g. breeding system in a semi-natural way, auto-produced feedstock within the farm and without the use of chemicals, re-use of livestock manure as fertilizer, machinery efficiency, small use of electricity in shed.

Outcomes demonstrate that analyzed breeding farms are well managed and clearly driven by a sustainable rationale. In general, not intensive breeding farms (e.g. semi-wild animals taken in grass-land and a limited time spent in cattle-shed) and organic feed (self-)production are good practices to mitigate carbon footprint and finally contribute to increase the overall quality of products. It is well known how products from breeding systems have high environmental impacts. Decreasing the consumption of these products, as a personal food attitude, is an obvious solution. Nevertheless, since these products are important for our nutrition, a desirable solution is also to choose higher quality food, such as products from Slow Food Presidia. The natural management of analyzed breeding farms allows for increasing quality and healthiness of food (besides good taste) and, as demonstrated above, also to mitigate environmental impacts and guarantee sustainability as prompted by the Slow Food Foundation.

References

1. Caro, D. et al. 2014. 'Global and regional trends in greenhouse gas emissions from livestock', Clim. Change 126, 203-216; **2.** http://www.fondazioneslowfood.com/ en/slow-food-presidia/; **3.** ISO 14040, 2006. Environmental Management-Life Cycle Assessment - Principles and Framework, **4.** ISO 14044, 2006. Environmental Management - Life Cycle Assessment - Requirements and Guidelines; **5.** IPCC, 2006. '2006 Guidelines for National Greenhouse Gas Inventories', (IGES, Japan, 2006); **6.** STELLA, 2005. 'STELLA and iThink Technical Documentation', Isee systems; **7.** Roma, R., et al., 2015. 'Life cycle assessment in the livestock and derived edible product sector', in 'Life Cycle Assessment in the Agri-food Sector: International Practices, Italian Experiences, Methodological Issues and Defining Practical Guidelines', Springer.

Hydrochemical and spatial analysis as tools to deciphrate groundwater flow: a case study in the central Alps

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The understanding of water flow in alpine catchment is a key issue in environmental analysis and planning, to have a clear concept of water distribution and availability and to monitoring water quality. So, although these settings are normally well supplied with precipitation and groundwater recharge, the water exploitation may represent a major challenge (1).

To understand water circulation there is the need to apply a multi-disciplinary approach, including a geological and geochemical understanding of the study area, the analysis of hydrochemical tracers, and statistical tools (as multivariate analysis and spatial analysis) to understand distribution of chemical variables and infer the possible groundwater flow (2).

In this study chemical analysis of water samples in a little catchment in the central Alps were statistically treated to understand similarities and dissimilarities between springs and to assess the possible groundwater circulation.

The study area analyzed includes two hydrological basins: the Ventina valley basin, principally alimented by the homonymous glacier, and the Pirola lake basin, alimented by atmospheric deposition and snow deposits. There are different lithologies in the two basins, because the Pirola lake is crosscutted by a fault separating metagabbros in the northern part (rich in minerals containing Mg, Ca, Al, K, Na) and serpentinites (containing elements as Mg, Fe, Ni, Cr, Cu) in the southern part (3).

Water samples were collected during summer 2014, 2015 and 2016. Chemical-physical parameters (pH, electrical conductivity and temperature) were directly measured on field using probes, and samples were collected to analyze for following analysis in laboratory for major ions (through ionic chromatography) and trace metals (through inductively coupled plasma-mass spectrometer). The collected data were then treated through multivariate statistics (using Principal Component Analysis and Cluster Analysis) and geostatistics (Moran's I for spatial autocorrelation and distribution mapping techniques) to observe differences and similarities to springs and model possible water circulation in the two basins. Moreover, the application of cluster analysis using different chemical variables show similarities in the different basins even if the underlying geology results different.

The results show that the distribution of different geochemical markers (as, for example, Ca/Mg ratio, K, Na), indicate similarities between springs of the two different basins, especially in the central area. The interpretation of data suggests so a possible communication, probably in the deep aquifer, from the different basins, indicating so a possible recharge of the Ventina valley even from the Pirola lake, and a mixing of the shallow and deeper aquifer.

This study remarks the need to apply multidisciplinary integrated approaches to understand natural phenomena as the water flow, even in a small and apparently simple structured basin.

References

1. Hilberg S. & Riepler F. (2016). Interaction of various flow systems in small alpine catchments: conceptual model of the upper Gurk Valley aquifer, Carinthia, Austria. Hydrogeology Journal, 24(5), 1231-1244; **2.** Voutsis N., Kelepertzis E., Tziritis E., Kelepertsis A. (2015). Assessing the hydrogeochemistry of groundwaters in ophiolite areas of Euboea Island, Greece, using multivariate statistical methods. Journal of Geochemical Exploration, 159, 79-92; **3.** Trommsdorff V., Montrasio A., Hermann J., Muntener O., Spillmann P., Giere R., (2007). The geological map of Valmalenco.

nZVI encapsulated in biochar from olive mill waste: production, characterization and application in removing pollutants from wastewater

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The work is focused on the production of carbon-encapsulated zero-valent iron nanoparticles (CE-nZVI) from moist biomass waste and their application in the removal of organic and inorganic priority pollutants from wastewater.

The nanoparticles are produced by Hydrothermal Carbonization (HTC), a process where the solution is heated in a high-pressure reactor at low temperatures from olive mill waste (OMW, a carbonaceous waste from the olive oil industry, very common in the Mediterranean area). OMW directly reacts with iron(III) (from Fe(III) nitrate nonahydrate salt), heated at 200°C for 3 hours.

A post-treatment with nitrogen increases the ZVI content, which is actively involved in the removal of heavy metals and pesticides from wastewater. In this work, different conditions of post-treatment are studied. In general, the total iron content increases with the temperature of post-treatment because of the increasing degree of carbon carbonization (temperatures of 600°C, 700°C and 800°C for 3 hours are tested). However, both the ZVI content and the surface area of the nanoparticles increase till 700°C and then they start to decrease, probably because at 700°C carbon still has an amorphous structure but at 800°C the surface of the particles becomes more crystalline.

The second part of the project is about the application, at lab-scale, of CE-nZVI in removing 5 heavy metals and a pesticide from an aqueous solution.

Regarding heavy metals, a solution containing chrome, cadmium, nickel, copper and zinc (10 mg/L each) is used. Metal ions are removed by sorption and reductive precipitation, according to their standard potential with respect to the iron's one. Results show that the problem of the aging effect (1) is solved using CE-nZVI instead of the not-encapsulated ones. In fact, no re-dissolution of any element is observed even after 200 hours.

The results of tests carried out using just OMW biochar (without ZVI) confirm that the presence of iron is essential for the removal of heavy metals.

The effect on pesticides is evaluated by experiments on a 100 mg/L aqueous solution of of 2,4-dichlorophenoxyacetic acid (2,4-D), a herbicide used worldwide to control the growth of broadleaf weeds, carried out with and without H_2O_2 and in the presence and absence of UV light. The removal mechanism involves the Fenton reaction, which produces highly reactive hydroxyl radicals that rapidly and unselectively oxidize non-biodegradable compounds. Best removal results are obtained using samples with 0.2 nFe/nC which is the maximum ratio that can be reached in CE-nZVI synthesis. The presence of hydrogen peroxide is fundamental for the formation of radicals. UV light improves the removal efficiency (photo-reduction produces more iron(II), which reacts to produce radicals).

In conclusion, the environmentally sustainable and low-cost production of CE-nZVI can contribute to solve the waste disposal problem, and the positive results at lab scale are promising for a future use of these nanoparticles in real plants for wastewater treatment.

References

1. Calderon, B., Fullana, A. (2015). Heavy metal release due to aging effect during zero valent iron nanoparticles remediation. Water Research, 83, 1-9.

Trace elements in a bioindicator and PM_{10}: are they correlated?

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The analysis of bark collected from the annual segments of the tree branches has shown an interesting potential as a natural archive, allowing to reconstruct the past deposition of the trace elements present in the atmosphere along a 10-15 year period (1). The results obtained are consistent with those reported in literature for different kinds of samples (e.g. particulate matter, dust, precipitation, aerosol, lichens).

Considering that part of the trace elements caught by the tree bark (and by other bioindicators) is associated to the particulate matter present in the atmosphere, the presented study aims to verify whether the PM_{10} values are correlated with the concentration of the trace elements measured in the bark of tree branches. In fact, data of PM_{10} have been collected during the last years in many cities, as the adverse effects of particulate matter on human health are well known (2).

What is rarely determined is the chemical composition of PM_{10}, although several recent studies have shown its relevance for health (3). Even when PM_{10} is analyzed, only the trace elements included in the legislative reference framework for air quality standards are measured.

In this work the concentrations of As, Cd, Co, Cu, Fe, Mn, Ni, Pb, V and Zn have been measured by ICP-OES on the bark of holm oak (*Quercus ilex* L.) branches (n=18) in the city of Genova. The annual segments (a total of 171 samples) cover the period from 2005 to 2016. These concentrations have been compared with the PM_{10} values measured by the monitoring stations managed by the Regional Agency for Environmental Protection (ARPAL).

Among the 10 elements investigated, significant correlations ($p<0.05$) with PM_{10} have been found for Cd, Ni, Pb and Zn, all elements having important effects on human health and often considered as produced by vehicular traffic.

The technique here described allows to obtain information about time periods or areas not covered by monitoring programmes and about trace elements never analyzed, because not considered important in the past.

The Authors acknowledge ARPAL for providing data of PM_{10}.

References

1. Drava G., Brignole D., Giordani P., Minganti V. (2017). *Env. Res.* 154: 291–295; **2.** WHO (2013). Review of Evidence on Health Aspects of Air Pollution – REVIHAAP Project. Technical Report. Copenhagen, WHO Regional Office for Europe; **3.** Schwarze, P.E., Øvrevik, J., Låg, M., Refsnes, M., Nafstad, P., Hetland, R.B., Dybing, E. (2006). *Hum. Exp. Toxicol.* 25: 559-579.

Advanced Diagnostic and Conservation: the case study of a chasuble dating from early 18th century

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The object of the study is a pink chasuble belonging to the ancient textile collection of the Palatine Chapel in Palermo, dating from early 18th century. It's a silky and metal polymateric artifact: gold and silver threads are embroidered or inserted in the fabric weaving (figure).

This kind of chasuble is called "Roman" and it's characterized by the presence of a central cross on the front and a central column on the reverse. These areas are made of embroidered satin while the rest of the artifact is made of a fabric called "lampas", probably a French production of the early 18th century, belong to the type of "lace fabrics".

The samples collected from an embroidered silk satin chasuble were analyzed using an innovative analytical approach. In the first phase of the work, a preliminary identification of the dyes present in the samples was performed through SERS on fiber analyses.

In recent years, surface-enhanced Raman spectroscopy (SERS) has emerged as a powerful alternative method for the study of organic colorants used in artworks. SERS is an ideal tool for the detection of dyes because it requires very little sample, enhancing Raman signals of analytes and quenching the typical fluorescence of organic compound. Generally, SERS analysis was performed on the extract of the sample and, only in the last few years, new SERS methods, based on direct SERS on fiber analysis without the need of extraction or hydrolysis pre-treatments, were developed (1). SERS on fiber methods result to be particularly interesting since strongly reduces the amount of sample required for dyes identification.

Then, in order to deepen the preliminary results obtained through SERS on fiber analyses, the dyes present in the samples were extracted using the innovative ammonia mild extraction method. The classic extraction methods were based on mixtures of organic solvent with acid (2,3,4). These methods imply the complete or partial hydrolysis of glycosidic compounds present in the samples, allowing only the identification of the main aglycones. The ammonia mild extraction method (5) was developed just for preserving the glycosidic compounds and then getting closer to the real molecule pattern involved in dyeing process. The results obtained allowed to identify the presence of several natural dyes (such as Madder, Brazilwood, Indigo, Quercitron and Saffron) and, only in one sample of a synthetic dye (Eosin), probably due to precedent restoration treatments.

References

1. A. Idone, M. Gulmini, A. H. Henry, F. Casadio, L. Chang, L. Appolonia, R. P. Van Duyned, N. C. Shah, *Analyst* 2013, 138, 5895; **2.** J. Wouters, *Stud. Conservation.* 1985, 30, 119; **3.** L. Valianou, I. Karapanagiotis, Y. Chryssoulakis, *Anal. Bioanal. Chem*. 2009, 395, 2175–2189; **4.** A. Manhita, T. Ferreira, A. Candeias, C. Barrocas Dias, *Anal. Bioanal. Chem.* 2011, 400, 1501–1514; **5.** L. Lombardi, I. Serafini, M. Guiso, F. Sciubba, A. Bianco *Microchemical Journal* 2016, 126, 373–380; **6.** S. Bruni, V. Guglielmi, F. Pozzi, *J. Raman Spectroscopy* 2011, 42, 1267-1281; **7.** M. Caycedo, *Identification of fifteen first priority textile dyes from the Schweppe collection with Raman and Surface Enhanced Raman Spectroscopy (SERS),* PhD thesis 2012.

Mesoporous substrates with ion-exchange functionalities for the removal of sugar matrices

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Sugars can be present in food products as native components or as added components during production processes.

From an analytical chemistry point of view, the presence of sugars can make difficult the routine safety control of food products (e.g. analysis of pesticides or other contaminants), whereas from an environmental chemistry point of view, sugars contribute to the increase of the biochemical oxygen demand (BOD) of wastewaters of food industrial processes.

Analysis of contaminants in food products is usually preceded by a sample pre-treatment to eliminate matrix interference and to separate analytes of interest from other components. QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) technique is one of the most used approach in food analysis. In this technique, sugar interference is removed by d-SPE using a commercial sorbent named PSA (primary, secondary amine).

The aim of this work is to prepare mesoporous substrates that can be used both as alternative sorbents to PSA in analytical chemistry applications and as adsorption substrates for the removal of sugar contribution to BOD.

For this purpose, a SBA-15 substrate was functionalized with (3-aminopropyl)-triethoxysilane (APTES) and N-3-trimethoxypropylaniline. The adsorption behaviour of the synthesized sorbents was tested on three representative sugars: glucose, sucrose and fructose. The effect of initial sugar concentration (5000-350000 mg/L), of the pH (2.1-8.5) and of the solvent in which sugars are extracted (water and acetonitrile) on the adsorption recovery is shown for each of the sugar molecule. The performances of the synthesized sorbent are compared with those of commercial PSA. To quantify sugar adsorption and to test the efficiency of the materials in real matrices, ion chromatography with amperometric detection was used.

For both the extraction solvent tested, the best performances were obtained at pH 2.1, with a contact time of one minute: these conditions are compatible with those of the QuEChERS technique. The adsorption of sugars obtained for both the materials is 10% -30% higher than the adsorption obtained with PSA, thus suggesting a possible replacement of commercial PSA in the QuEChERS technique with the substrates proposed.

To verify the performances of the substrates in food matrices analysis, we applied QuEChERS extractions on strawberries intentionally contaminated with PAHs and PCBs. After extraction, PAHs and PCBs were analysed by GC-MS. Signal-to-noise ratio and method detection limits were calculated for samples treated with PSA and samples treated with new materials synthesized.

The suitability of the sorbents on the reduction of the organic load of industrial wastewaters was finally tested, simulating the typical composition of wastewater of soft drinks production. The two proposed materials show better performance than PSA: glucose, sucrose and fructose removal was about 90% for SBA-15 functionalized with N-3-trimethoxypropylaniline, 70% for SBA-15 functionalized with APTES and 60% for PSA.

Micro-invasive study of a 15th century Armenian manuscript: first identification of lac dye by means of HPLC-MS

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The possibility of analyzing small samples taken from paintings allows obtaining interesting information that could not be gained by means of non-invasive techniques. This is particularly true for illuminated manuscripts, which are fragile and precious artworks and for which sampling is therefore usually not allowed. In such cases the knowledge of the colourants used for the miniatures is forcedly confined to the results yielded by a poorly selective non-invasive analytical approach.

In the present case, a 15th century Armenian illuminated manuscript was subjected to a diagnostic study. The manuscript was made in a scriptorium at Aghtamar Island, in the Vaspurakan region of historic Armenia and the present investigation represents one of the few performed on ancient Armenian manuscripts. A selection was carried out in order to obtain samples from all hues present in the miniatures and 15 micro samples (mostly < 1 mm^2) were obtained. The samples size was still suitable for performing non-destructive measurements with UV-Visible diffuse reflectance spectrophotometry with optic fibers (FORS), in order to obtain preliminary information useful for addressing further analyses. After that, Raman spectroscopy, Surface Enhanced Raman Spectroscopy (SERS), SEM-EDX and HPLC-MS were used for a complete characterization of the samples.

The combination of molecular (Raman, SERS, FORS, HPLC-MS) and elemental (SEM-EDX) techniques allowed the identification of all the colorants used in the miniatures. Natural ultramarine blue, indigo, cinnabar, minium and orpiment were the main identified pigments. Green hues were rendered by a mixture of indigo and orpiment, the so-called *vergaut*. Of particular interest was the identification of iron-gall ink, which in this case has been used as a pigment in the black areas of the paintings.

As to red-pink areas, preliminary FORS analysis suggested the presence of dyes from scale insects such as kermes, Armenian cochineal, Polish cochineal or lac dye (Indian lac), whereas Mexican cochineal was excluded for historical reasons. This analysis, however, is not selective enough to distinguish among these colourants which belong to the class of anthraquinonic dyes. Despite the extremely small size of the available sample, upon hydrolysis with concentrated formic acid and HPLC-MS analysis it was possible to identify lac dye through the identification of laccaic acid A and B. Lac dye is obtained from *Kerria lacca*, a species native of Southeastern Asian countries, therefore its presence - and not that of Armenian cochineal - might seems unusual from the geographic point of view. Nevertheless, the exhaustive molecular characterization obtained here for the organic dyes is relevant as miniature paintings are very rarely analyzed with invasive techniques and such information is therefore almost totally lacking.

Interesting information was also obtained regarding later interventions on the miniatures. Raman analysis highlighted the presence of 20th century pigments such as phthalocyanine blue and Naphthol Red, clearly indicating contemporary restorations.

Morphochemical characteristics and mixing state of long range transported wildfire particles at Ny-Ålesund (Svalbard Islands)

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Wildfires are an important variable of climate change in the Arctic as a source of particles which are able to modulate the radiative forcing in the atmosphere and the albedo properties of snow and ice exposed surfaces besides serving as large sources of cloud condensation nuclei (1,2). Recent studies on the mineral chemistry and geochemical signature of aerosols sampled at ground level and along vertical profiles at the scientific Polar base of Ny-Ålesund, Svalbard Islands (78°55'30"N 11°55'20"E), have shown a significant contribution of biomass burning forest fire on this area especially in summertime (3,4). A prolonged and exceptionally intense air mass advection event transporting biomass burning aerosols generated in Alaska affected Ny-Ålesund in the mid of July 2015. This study is focused on the morphochemical characteristics and mixing state of individual aerosol particles collected during the event. To this aim aerosol samples were collected on nucleopore polycarbonate membranes using a DEKATI 12-stage low volume impactor and analyzed by scanning electron microscopy (SEM) coupled with image analysis, 3D surface reconstruction and energy-dispersive X-ray microanalysis (SEM-EDS). Results of SEM investigations depict a complex aerosol characterized by an external mixing between a main part of carbonaceous organic particles (tar balls – TBs - and organic particles - OPs), lower ammonium sulfate (AS) and minor potassium chloride (KC) and mineral dust (MD) amounts. The carbonaceous particles, in particular, are mostly in the accumulation mode size range with morphologies that range from spherical to slightly elongated. The organic particles show an internal mixing of low density organics and/or ammonium sulfate upon denser nuclei. Individual particle analyses were complemented by aerosol size distribution (Aerodynamic Particle Sizer, Scanning Mobility Particle Sizer) and optical (Particle Soot Absorption Photometer, nephelometer) measurements at ground level in order to retrieve the optical and radiative properties of the aerosol in the atmosphere and to predict the fate and behaviour of particles upon deposition at ground level. Individual particle analyses were also compared with bulk chemical analyses on daily sampling filters and back-trajectory analyses of the air mass movement in order to enucleate distinct sources of the aerosol during the long range transport (5).

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References

1. Spracklen, D.V., Carslaw, K.S., PöschlU., Rap, A., Forster, P.M. (2011) Atmos. Chem. Phys. 11, 9067-9087; 2. Liu, Y., Goodrick, S., Heilman, W. (2014) Forest Ecol Manag 317, 80-96; **3.** Giardi, F., Becagli, S., et al. (2016) Rend. Fis. Acc. Lincei 27, doi:10.1007/s12210-016-0529-3; **4.** Moroni, B., Cappelletti, D., et al.. (2016) Rend. Fis. Acc. Lincei 27, S115–S127. 5. Moroni B., Cappelletti D., Crocchianti, S., Becagli, S., et al (2017) Atmos. Environ., 156, 135-145.

TiO_2-NPs supported on sepiolites: a photocatalytic tool for removal of emerging pollutants

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Heterogeneous photocatalysis can be applied to several research areas, especially for environmental applications; among these, water remediation and wastewater bleaching are important fields the scientific research is focusing on. Nanometric TiO_2 is one of the most preferable material, due to its strong oxidizing ability, excellent chemical stability, long durability and reusability, non-toxicity, low cost and high surface to volume ratio. Due to its small particle size, the use of bare TiO_2 is limited, indeed, because it is difficult to be recovered from the suspension medium. A possible way to overcome this limitation is using a supporting material for TiO_2 with similar chemical and physical properties, such as chemical stability, reusability, water insolubility and high surface-to-volume ratio (1). Due to its high adsorbent capacity, sepiolite was chosen as supporting material for undoped and N-doped anatase TiO_2. Starting from a sol-gel route, where 2-propanol, titanium tetraisopropoxide and water or an ammonia solution were mixed together (1:2:5, V/V) in order to obtain an amorphous gel of undoped TiO_2 or N-doped, respectively, a solid-state and a hydrothermal synthesis were performed to support the nanometric TiO_2 onto the sepiolite. A chemometric approach was adopted in order to find the best syntheses conditions among the variables investigated, which are reagents ratio, temperature and time. This coupled system has potential application in the removal of organic emerging pollutants, being particularly effective in the treatment of contaminated water with pharmaceutically active compounds, whose presence in the environment represents an increasing threat (2). Photocatalytic experiments were performed on the optimized samples on methylene blue and on Ofloxacin solutions (a fluoroquinolone antibiotic), under simulated solar light and reaching very high degradation values (figure 1).

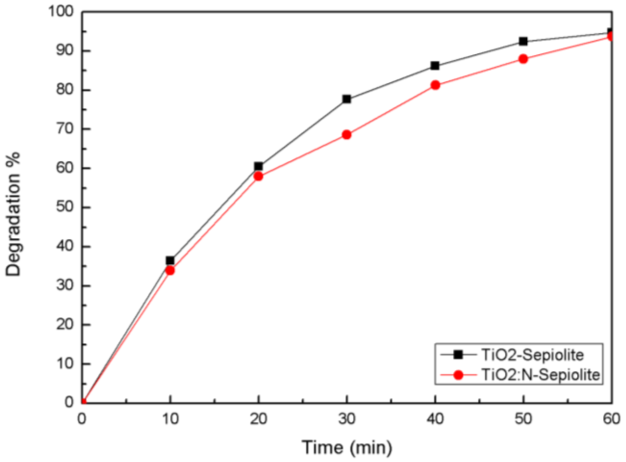

Figure1: Percentage degradation of TiO_2 and N-doped TiO_2 of an aqueous solution of methylene blue.

References
1. Uğurlu M.; Karaoğlu M.H. Chem. Eng. J. 2011, 166, 859-867; **2.** Villa S.; Caratto V.; Locardi F.; et al. Materials 2016, 9, 771.

Simultaneous determination of Chlorinated Priority Organic Pollutants (e.g. PCB, PBDE, PCDD, PCDF) in soil and sediments by Gas Chromatography-Tandem Mass Spectrometry

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Epidemiological studies show that exposure to specific persistent organic pollutants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF), polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) is strongly associated with negative interferences on endocrine systems and on alterations of reproductive physiology. Therefore, the determination of these compounds in the environment is of great importance from the ecotoxicological point of view. Accurate determination of PCDD/F, PBDE and PCB in complex matrices is a challenge because of their low expected concentrations in the range of ppb to sub-ppb. For the complexity of environmental matrices, analytical determinations often require long time periods of analysis and several stages of extraction/preconcentration, purification, etc in order to eliminate interferences. These procedures do not fit in extensive environmental monitoring programs, where it is necessary to analyze a large number of samples at a time not excessively long. In this paper, the official EPA methods (1,2) for chlorinated pollutant analysis has been evaluated and modified to provide a faster and more reliable alternative analytical method for simultaneous determination of interest compounds in soil and sediments with a single extraction.

Accelerated solvent extraction (ASE) has been used for simultaneous extraction of organic compounds. The most favorable extraction conditions proved to be n-hexane as the extraction solvent, temperature of 120 °C, pressure of 1500 psi and three static cycles in each case. Purification of the extract was accomplished by automated Power-Prep^{TM}/Sample Clean-up system. The analyses were then performed by using gas chromatography coupled to triple quadrupole mass spectrometry. Utilizing triple quadruple mass spectrometry under positive EI with multiple reaction monitoring (MRM) mode, greatly enhances the sensitivity and selectivity of detection, compared to selective ion monitoring (SIM) mode. The GC-QqQ(MS/MS) sensitivity, lower than that of GC-HRMS, is good enough (LODs in the down to low pg levels) to detect the normal concentrations of these compounds in environmental samples. The obtained analytical results demonstrate excellent recoveries for the various congeners, comparable to those of official methods and detection limits useful for the analysis of real matrices. The determination of these compounds in soils and sediments and the evaluation of the distribution of various congeners (fingerprint method) has allowed to obtain information on the origin of the contamination.

References

1. EPA Method 1613 revision B (1994), Tetra-through octa-chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS; Soxhlet Method 1613, Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, October 1994, p.86; **2.** EPA Method 8290a: Polychlorinated Dibenzo-P-Dioxins and Polychlorinated dibenzofurans by High-Resolution Gas Chromatography/High resolution Mass Spectrometry (HRGC/HRMS), February 2007, 72 p.

Use of "mussel watch" experiments in biomonitoring of heavy metal and PAHs in a Site of National Interest

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Biomonitoring represents a useful tool for quantifying and clarifying the current status of environmental health, and indirectly assessing coastal water quality and changes in the environment, generally due to anthropogenic causes. In addition, it plays a key role in the formulation of protocols for vulnerable marine ecosystems, such as coastal and estuarine areas, transitional waters, influenced by various anthropic activities. Monitoring programmes use a great number of bioindicators - "sentinels organisms" - to detect temporal and spatial variation of marine contamination (1). As intertidal filter feeders, mussels accumulate heavy metals and organic pollutants in their tissues in proportion to the degree of environmental contamination. Bioconcentration factors depend not only by environmental conditions but also by physiological parameters such as the reproductive stage of organisms (2).

In order to evaluate metals and Polycyclic Aromatic Hydrocarbons (PAHs) bioaccumulation, mussel watch experiments were carried out using bivalve molluscs (*Mytilus galloprovincialis*) in contaminated areas of the Mar Piccolo of Taranto (Ionian Sea, Southern Italy), classified as "Site of National Interest" established by National Law 426 (1998) and included in the "National Environmental Remediation and Restoration Projects.".

All mussels with 40-60 mm shell size were purchased from aquaculture farm located in a clean site on the Adriatic coast during the pre-spawning period in order to control seasonal variation due to mussel physiology (1).

Mussels were analyzed (T=0) and put into net cages that were suspended in the water column in two stations of the first Inlet in Mar Piccolo of Taranto. Every fifteen, mollusks were sampled by a scuba for a ten-week period, to carry out laboratory analysis.

The results showed the increase of PAHs and metals concentrations over time. For example, at the end of the exposure, mercury concentration, in molluscs increased by three times compared to baseline. Concerning ΣPAHs, after 5 week the concentration increased by about three times compared to T=0.

The obtained results have also made it possible to determine important correlations with the degree of contamination of marine sediments and to point out that resuspension phenomena of contaminated sediments in coastal areas can be a main source of contamination.

These data show that the "biota" (mussels in this case) is still a relevant target of exposure to some contaminants; for this reason, the biomonitoring activities are very important tools for human health and ecosystem risk assessment.

References
1. Carro N. et al., 2004, "Efficient Possible influence of lipid content on levels of organochlorine compounds in mussels from Galicia coast (Northwestern, Spain). Spatial and temporal distribution patterns." Environment International, 30, 457-466; **2.** Cardellicchio N. et al., 2010. "Preliminary results of pollutants biomonitoring in coastal marine and transitional waters of Apulia Region (Southern Italy).", Fresenius Environmental Bulletin, 19 (9), 1841-1847.

Towards a closure of the European copper cycle: scenarios and environmental implications

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The scarcity of natural deposits has constrained Europe to import large amount of primary copper (Cu) forms to meet the domestic demand. In the recent years, warnings have risen up due to the risk of potential restrictions to the global primary Cu supply: ore grade decrease and a lack of potential substitutes can affect the future use of this metal (1,2). Consequently, the European Commission has promoted recycling as a central mean to secure raw material inputs to the European industry. To support the efforts of changing a respectable recycling rate (i.e., 60%) but far from perfect performance, we have explored four possible scenarios of Cu demand and supply to 2050 in the EU-28 and provided the related potentials for energy savings and climate change mitigation.

The study builds upon previous results (3) and applies linear regression analysis to compute the best fitting equations based on the major explanatory variables of Cu demand, including population, gross domestic product, the level of urbanization, and the time as explanatory parameter to capture the effect of time-dependent variables (e.g., technological development). The four scenarios model growth rates for the set of explanatory variables to 2050 according to their storylines (4).

The set of scenarios describes four possible futures, including (i) a future world driven by market forces in which per capita resource consumption continues to increase proportionally with those of the more developed countries (named Market World, MW); (ii) a scenario similar to the MW but in which a transition to a world more respectful of the environment is driven by government policies (Toward Resilience, TR); (iii) a world in which security is set as top priority and determines restriction of people migration and international trades (Security Foremost, SF); (iv) a world driven by the Sustainable Development Goals that determines more social, economic, and environmental equitability (Equitability World, EW), (4). The material flow model developed in (3) is used to simulate the generation of Cu scrap at end-of-life based on the expected future demand. Finally, we applied life cycle assessment to estimate the energy savings and carbon emission results associated to Cu recycling in the region. To this end, each scenario models developments in the energy inputs to Cu production and in the electricity production mix.

The results show that the current pattern of Cu production and consumption, as exemplified by the Market World scenario, is hardly sustainable in the long term: intensive inputs of primary Cu will be required and secondary Cu supply will represent only 45-50% of the demand, if recycling performance continues at the current levels. Aggressive recycling (i.e., 90% collection rate and 90% recovery rate) would likely improve the situation only by a little. The Equitability World is the only scenario that is highly positive even in case of stationary recycling rates. Prospects for environmental benefits follow the order EW > SF > TR > MW. Compared to the present demand (i.e., 2014), the resulting potentials for climate mitigation are expected to reduce the carbon footprint of Cu demand by about 25% to 42% depending on the scenario. Aggressive recycling would increase the benefits up to 35% to >60% for the EW. Energy savings are modeled to enhance by 5 to 10 times the present situation (i.e., ~40 TJ in 2014), should the ore grade decrease be confirmed. The study is part of the "QUEMC" project, which has received funding under the Marie Sklodowska-Curie grant agreement No 704633, and we expect that it can contribute significantly to the circular economy debate for strengthening guidance in the European climate strategies.

References

1. Vieira, M.D.M., et al. Environ. Sci. Technol., 2012, 46, 12772-12778; **2.** Graedel, T.E., et al. Criticality of metals and metalloids. PNAS, 2015, 112, 4257-4262; **3.** Ciacci et al. Resources, 2017, 6(1), 6; **4.** United Nations Environment Programme (UNEP). Global Environmental Outlook 4: Environment for Development. United Nations Environment Programme, 2007, Nairobi, Kenia.

Thermal stability and evolved gases investigations of all-inorganic lead halide perovskite $CsPbX_3$ (X= Cl, Br, I) nano-cubes for optoelectronic applications.

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The research of new optoelectronic materials is increasingly attracted on new quantum dots (QDs), the best nanocrystals (NCs), in terms of size, shape and composition, are binary and multinary (ternary, quaternary) metal chalcogenide (1). The all-inorganic lead halide perovskite, $CsPbX_3$ (X=Cl, Br, I), exhibit huge potential in various optoelectronic devices, due to the unique optical properties, i.e. size-dependent emission wavelength, narrow emission spectrum, and high luminescent efficiency. The practical advantage of $CsPbX_3$ NCs is the facile access to the visible spectral region *via* one-pot synthesis (2) as reported in Figure 1. The method allows to obtain monodispersed $CsPbX_3$ NCs having cubic shape and size around 10 nm. To date, the main studies are carried out to identify and improve the optical properties, in function of the influence of the thermal treatment on systems based on $CsPbBr_3$ nano-ink (3). Here we report a study about the stability of $CsPbX_3$ (X=Cl, Br, I) cubic nanocrystals performed through differential thermal analysis/thermogravimetry (DTA/TG) coupled with gas chromatography – mass spectrometry (GC-MS), in order to determine the degradation mechanism and the properties after an *in-situ* annealing.

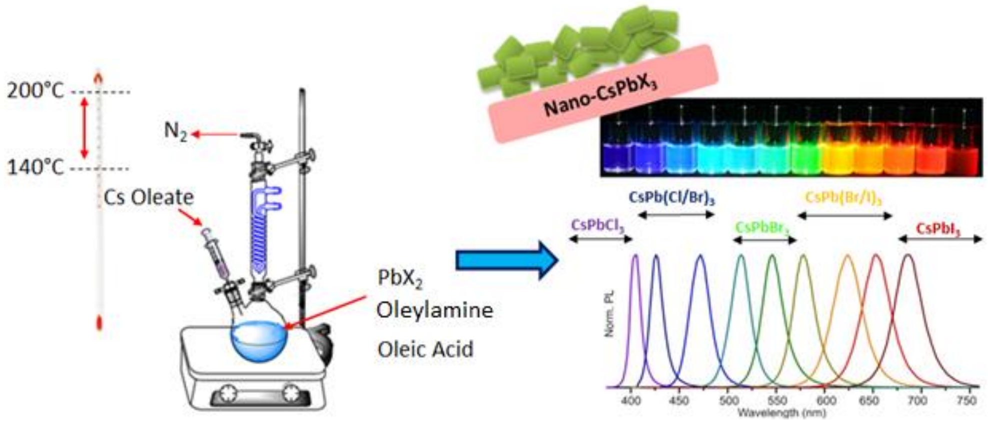

Figure 1.Scheme of one-pot synthesis of all-inorganic halide perovskite and relative optoelectronic properties (1)

References
1. L. Protesescu, S. Yakunin, M.I. Bodnarchuk, F. Krieg, R. Caputo, C. H.Hendon, R. Yang, A. Walsh, M. V. Kovalenko. Nanocrystals of cesium lead halide perovskites (CsPbX3, X=Cl, Br, and I): Novel optoelectronic materials showing bright emission with wide color gamut. *Nano Letters*, 2015, 15 (6), 3692–3696; ***2.*** *S. Yakunin, L. Protesescu, F. K. Maryna, I. Bodnarchuk, G. Nedelcu, M. Humer, G. De Luca, M. Fiebig, W. Heiss, M. V. Kovalenko. Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites.* Nat. Commun, 2015, 6, 8056; **3.** F. Palazon, S. Dogan, S. Marras, F. Locardi, I. Nelli, P. Rastogi, M. Ferretti, M. Prato, R. Krahne, L. Manna. From $CsPbBr_3$ nano-inks to sintered $CsPbBr_3$-$CsPb_2Br_5$ films via thermal annealing: implications on optoelectronic properties. J. Phys. Chem. C. DOI: 10.1021/acs.jpcc.7b03389.

GOLENA BLU
Environmental improvement intervention in the industrial area of Tolmezzo Sud (UD) Technical-practical aspects, didactic purposes and growth for the territory

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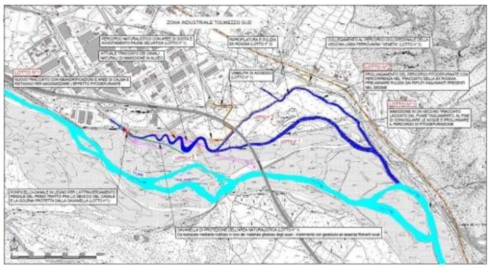
The project aims at improving the environmental situation in the industrial area of Tolmezzo Sud where the waste water is discharged by the consortium water treatment plant, before entering the Tagliamento River.

Over the last years the natural evolution of the riverbed, the alternating of lean and flood times (1,2,3,4) and the water coming from a local canal have led to the creation of a floodplain. This stretch of floodplain, affected by the discharged waste water, has assumed a wiggly configuration; thus slowing down the river flow speed and enhancing the favorable growth of typical wetland and cane plants which have self-depurative properties in themselves. The main aim of the project interventions is to amplify the natural situation that has recently emerged after the installation of the wastewater treatment plant. The proposed intervention, given the limited vital flow of the watercourse, includes:

- Increasing the twisted floodplain tract to expand the wet surface, active in the plant-based wastewater-treatment
- Growing additional plants with purifying effects and extending the vegetated surface for a boosted water purification (5)
- Raising awareness among the community of the environmental issues through the realization of a nature and educational trail within the naturalized area
- Disseminating the potential of mitigating measures
- Promoting the project TOLMEZZO - CITTA 'ALPINA 2017, with a concrete impact on the territory for the whole community and for the development of areas with strong anthropic pressure, by means of a reconversion of the river to its natural state.

Area of intervention Tolmezzo (UD)



Global project view “Golena Blu”

References

1. Piano Regional Protection of the waters of the FVG Regional Technical Attachments Cartography and Relationships,WEB GIS REGION FRIULI VENEZIA GIULIA; **2.** Management of measurements and monitoring of the flows of watercourses, groundwater levels and aquatic biocenosis within the River Tagliamento mountain range.Final Report - Central Environment and Public Works Hydraulic Service - Hydrological Operational Unit; **3.** Rainfall and Flow Measures of the Tagliamento River Basin provided by the FRIULI VENICE GIULIA; **4.** Hydrographic data of the Tonini-Pulselli River Tagging River Basin - Electric Power n.10-1971; **5.** Technical Guide for Designing and Managing Fertilization Systems for Urban Wastewater Treatment. Council of the Federal Council of 05/04/2012 ISPRA - Institute for the Protection and Environmental Research Via Vitaliano Brancati, 48 - 00144 Rome.

Reproducibility and stability over time of silver colloidal pastes for Surface Enhanced Raman Spectroscopy (SERS) of natural dyes in ancient artworks

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Surface-Enhanced Raman Scattering (SERS) using noble metal nanometric surfaces represents an ideal analytical technique to detect and identify dyes in artworks (1), due to the dramatic enhancement of the Raman signals together with fluorescence quenching with respect to traditional Raman spectroscopies. Ag colloids are among the most popular SERS substrates employed in the detection of dyes in samples from the cultural heritage domain. One of the procedures to synthesize Ag substrates was proposed by Lee and Meisel and uses silver nitrate as Ag precursor and sodium citrate as reducing agent. The synthesis can be followed by an aggregation of the Ag nanoparticles through centrifugation of the colloid, obtaining the so-called 'silver colloidal pastes'. These pastes have been successfully used to obtain direct SER spectra of dyes from a number of materials, with the advantage of being effective in obtaining signals from very small samples without the need of complex preliminary treatments.

An inherent characteristics of the SERS technique is the variable intensity of the SER signals. Accordingly, the recent research activities of our group in the field of SERS analysis of dyes in archaeological and historical samples (2,3) evidenced a certain variability of the SERS response for different Ag paste batches. Moreover, for a same Ag paste batch, it has been highlighted that the SERS behavior is not constant over time. Furthermore, the synthesis procedure is relatively time consuming and cannot be realized on a very small scale. Thus, following the behavior of the Ag pastes over time would be very helpful in obtaining more controlled and reproducible results and in reducing any possible wastefulness. Considering all these factors, the synthesis of different Ag paste batches was carried out to evaluate: 1) the aging effect on the SER spectroscopic response of the pastes, by acquiring spectra on the same batch at different times (up to 10 weeks), 2) the reproducibility of the SER spectroscopic response of the pastes within the same batch (*intra-batch*) and among different batches (*inter-batch*) at the same aging time, 3) the use of an alternative synthesis procedure (by using ice at the end of the chemical reduction thermal step) and 4) the comparison of the spectroscopic response obtained on samples prepared with the same Ag paste at different aging times with those on the same sample prepared with the newly synthesized paste and acquired at the same aging times.

For considering the above reported points, we evaluated the spectroscopic response of the Ag pastes - as signals of Ag and citrate are normally obtained - and SER signals of a wool sample dyed with cochineal.

As expected, the overall results confirmed that it is not possible to obtain a completely predictable enhancement. Notwithstanding, they allow drawing some important conclusions. First of all, the results indicated that the paste efficiency reaches a maximum after some time from its synthesis. Moreover, they gave precious indications on the optimal sample preparation procedure and guarantee the analysis of the samples even after several weeks from the preparation.

References

1. F. Casadio, M. Leona, J.R. Lombardi, R. Van Duyne. Identification of organic colorants in fibers, paints, and glazes by surface enhanced Raman spectroscopy Acc. Chem. Res. 2010, 43(6), 782-91; **2.** M. Aceto, E. Calà, A. Arrais, M. Clericuzio, F. Marsano, A. Idone, P. Davit, L. Menghini and M Gulmini. On the identification of folium by SERS: from crude extracts to illuminated codices. J. Raman Spectrosc. 2017, 48, 530–537; **3.** A. Idone, M. Aceto, E. Diana, L. Appolonia, M. Gulmini, Surface-enhanced Raman scattering for the analysis of red lake pigments in painting layers. J. Raman Spectrosc. 2014, 45, 1127–1132

Cobalt beta zeolite catalyst for the trichloroethylene oxidation

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Trichloroethylene (TCE) is a halogenated aliphatic organic compound frequently detected as pollutant in the atmosphere and also in soils and groundwater (1). In the last years, several strategies have been developed for the removal of TCE including adsorption processes, phytoremediation and thermal incineration. Catalytic oxidation of TCE is an interesting alternative that permits to operate at lower temperatures (250–550 °C) with a drastic reduction of energetic costs (2). In the last years the activity of beta zeolite loaded with transition metals in the catalytic oxidation of trichloroethylene was evaluated (3). In this work Co-beta zeolite was prepared by pore volume filling method and it was tested for the total oxidation of gaseous TCE. Moreover the effect of water vapor (1.0 %) on the catalysts activity and selectivity was also investigated. Experiments were carried out in a fixed bed reactor (4).

Thermal oxidation, performed without catalysts, have shown a low TCE conversion under 600 °C. On the other hand, when using Co-beta zeolite as catalysts for the TCE oxidation the conversion starts at 250 °C, achieving T_{50} and T_{90} respectively at 400 °C and 450 °C. Moreover the addition of water to the feed stream only slightly reduces the activity observed under dry air conditions. Product distribution in the TCE oxidation reaction for dry and wet conditions were reported in Figure 1a and 1b.

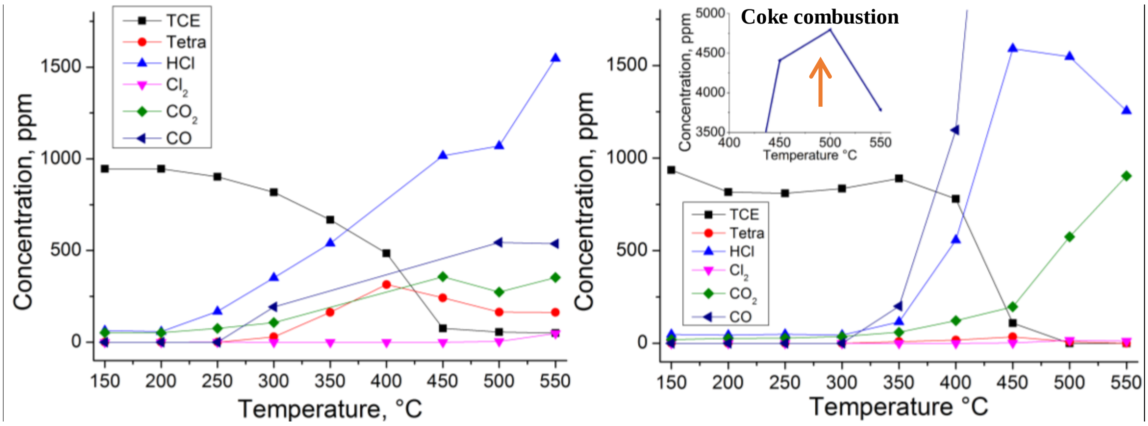

Fig. 1a/b Product distribution in the TCE oxidation reaction over Co beta zeolite for dry (right) and wet (left) conditions ([TCE]= 1000 ppm, 400 mL/min, 0.7 g of catalyst) .

Nevertheless, the presence of water vapor significantly increase the production of CO (inset shown in Fig. 1b). These results can be explained by a competitive absorption mechanism on the zeolite surface; due to its polarity, water competes for the absorption on the zeolite surface resulting in a lower oxidation activity of the catalyst and in an inhibition of tetrachloroethylene production. The last can be explained by a reduction of the zeolite acidity responsible of trans-chlorination reactions. From this work we can conclude that Co-beta zeolite is an active catalyst in the TCE oxidation of Moreover the presence of water vapor slightly reduce the catalyst activity being most significantly its influence in the selectivity of the reaction.

References
1. F. Rossi, R. Cucciniello, A. Intiso, O. Motta, N. Marchettini, A. Proto (2015) AIChE J. 61, 3511-3515; **2.** R. Cucciniello, A. Intiso, S. Castiglione, A. Genga, A. Proto and F. Rossi (2017) Appl. Cat. B: Environ 204, 167-172; **3.** N. Blanch-Raga, A.E. Palomares, J. Martínez-Triguero, S. Valencia (2016) Appl. Cat. B: Environ. 90–97; **4.** N. Blanch-Raga, A.E. Palomares, J. Martínez-Triguero, M. Puche, G. Fetter, P.Bosch, Appl. Catal. B: Environ. 160 (2014) 129–134.

Use-wear traces and wood tar residues on Funnel Beaker culture flint harvesting tools: a case study from south-west Poland

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Prehistoric harvesting tools made from lithic materials are easily distinguished amongst the archaeological assemblages. Lithic sickle inserts bear macroscopically visible traces of use. Cutting cereals causes edge rounding and highly reflected polish with flat topography cut through striations of various frequency (1). However, a location of polish and other associate traces show only which part of a lithic specimen served as a working edge, but the reconstruction of a complete sickle is not possible. More data, such as handles or residues of glue - wood tar or pitch - are necessary.

The technology of manufacturing adhesives for hafting arrowheads and projectiles had been known as early as in the Palaeolithic (2) and the Mesolithic (3). From the Neolithic European sites whole lumps of wood tar or post-production residues inside vessels or spoons are reported (4). The use of wood tar or pitch for hafting stone or bone tools by the Neolithic people is less documented. So far, no flint artefacts with macroscopically visible resinous substances are reported from SW Poland. The only proof of wood tar production in the Neolithic in this part of Poland are the remains of probably tar kiln with charred birch bark in the bottom (5).

Microscopic use-wear analyses of flint tools from the archaeological site Polwica-Skrzypnik in south-west Poland, dated back to the Funnel Beaker culture (TRB, late Eneolithic), revealed brawn or blackish substances on the surfaces of a few retouched blades. Specimens had been used for cutting cereals or other siliceous plants. The combined Fourier Transform infrared spectroscopy (FTIR) and gas chromatography coupled with mass spectrometry (GC-MS) study showed that dark substances are residues of wood tar or pitch - adhesives used for hafting. For the first time flint artefacts with macroscopically visible resinous substances are reported from this part of Poland. Resinous matter covers almost whole surface of tools. Location and distribution of use-wear traces clearly show that tools were used in longitudinal motion. Microscopic study together with residue analysis reveal the manner of use of the late Eneolitic sickles and the hafting mode

References

1. Gijn, A.L. van, 2010, Flint in focus. Lithic Biographies in the Neolithic and Bronze Age. Sidestone Press, Leiden; **2.** Colombini M. P., Modugno F., Ribechini E., 2006, Rapid Communications in Mass Spectrometry, 20, 1787-1800; **3.** Aveling, E., Heron, C., 1998, Ancient Biomolecules, 2(1), 69-80; **4.** Pietrzak, S., 2010, Archaeologia Bimaris, Monografie, tom 4, Wydawnictwo Poznańskie, Poznań; **5.** Wojciechowski, W., 1969, Sprawozdania Archeologiczne, 21, 29-39

ToF-SIMS technique applied to the study of organic and inorganic components in cultural heritage studies

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Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a powerful method to investigate the surface composition of materials. Here we focus on the application of ToF-SIMS to study the inorganic components and the organic binders used in cultural heritage artworks (1,2). ToF-SIMS was applied to identify the pigments as well as the protein-based binders used in paintings of the 14 and 15th century on wooded panels and on walls. The results of ToF-SIMS, combined with those of other micro analytical techniques, allow to obtain a thorough characterization of the painting layers. Thanks to the spatial resolution of ToF-SIMS, it is possible to analyse, on the same sample, the priming and painting layers. A principal component analysis (PCA), based on the comparison of data of painting samples with those of artificially aged organic binders as references, is needed to characterize organic components in the painting layers. The ToF-SIMS analysis permitted to identify the organic binders present in the paintings and to study the ageing mechanisms of these protein-based matrices.

References
1. A. Atrei, F. Benetti, S. Bracci, D. Magrini and N. Marchettini: “An integrated approach to the study of a reworked painting “*Madonna with Child”,* attributed to Pietro Lorenzetti"; Journal of Cultural Heritage, 15(1), 80-84 (2014). DOI: 10.1016/j.culher.2013.01.009. **2.** A. Atrei, F. Benetti, E. Gliozzo, G. Perra, N. Marchettini: “Chemical characterization of protein based binders in painting samples by means of ToF-SIMS: Tests on ancient and model samples”, International Journal of Mass Spectrometry, 369, 9-15 (2014). DOI:10.1016/j.ijms.2014.05.001.

Synthesis, characterization and applicative study of innovative materials for the conservation of cellulosic artefacts

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The interest of academia and industry for the use of renewable resources, in particular lignocellulosic biomasses, as an alternative to oil for the production of energy, fuels but also of new chemicals has grown in recent years. Moreover, focusing on the conservation of cultural heritage, the use of bio-based materials has further advantages like the compatibility, the affinity and the respect for the works of art, especially those made of the same chemical species that constitute the biomass (i.e. wood and paper) (1,2).

In this research new biopolymers and nanocomposites were synthesized using saccharides as feedstocks and their application in the conservation of cellulosic artefacts was studied. Saccharides were chosen as starting materials in order to introduce in the final products units with a structure similar to that of the cellulosic substrate and the synthetic methodologies were selected taking into account the principles of the Green Chemistry and the future application in the preservation of the cultural heritage. Allyl saccharide monomers were synthesized using allyl bromide to functionalize trehalose and glucose, obtaining products whose degree of functionalization varies according to the molar ratio between the reagents. The bio-based monomers were used for the synthesis of vinyl acetate copolymers, leading to the obtainment of final products that are soluble in acetone, but only partially soluble in water, according to the ratio between the comonomer units in the chains. In order to obtain water soluble products suitable to be used in the treatment of wood and paper and to prevent the hydrolysis of the vinyl acetate groups after the application on the degraded material, the vinyl acetate copolymers were hydrolysed to the correspondent vinyl alcohol copolymers, that were studied as consolidant for waterlogged archaeological wood. Real wooden samples were treated and the results were compared to those obtained using other bio-based oligoamidic products, which had been previously studied (2). The affinity of the products for wood and the reversibility of the treatments were evaluated together with some physical properties of the treated wood (i.e. maximum water content, basic density and volumetric shrinkage).

Finally, new nanocomposites between TiO_2 anatase nanoparticles and allyl saccharide/vinyl acetate copolymers were obtained by grafting the copolymers on properly functionalized nanoparticles. The nanocomposites were designed with the aim of obtaining new products with antimicrobial activity for the superficial treatment of cellulosic artefacts. An applicative study was performed to evaluate the antimicotic effect of the nanocomposites on recent wood against the attack of the fungus *Trametes versicolor*.

References
1. G. Cipriani, A. Salvini, P. Baglioni, E. Bucciarelli *Journal of Applied Polymer Science*, 2010, *118*, 2939; **2.** G. Cipriani, A. Salvini, M. Fioravanti, G. Di Giulio, M. Malavolti *Journal of Applied Polymer Science*, 2013, *21*, 1.

LCA as suitable tool to improve industrial processes

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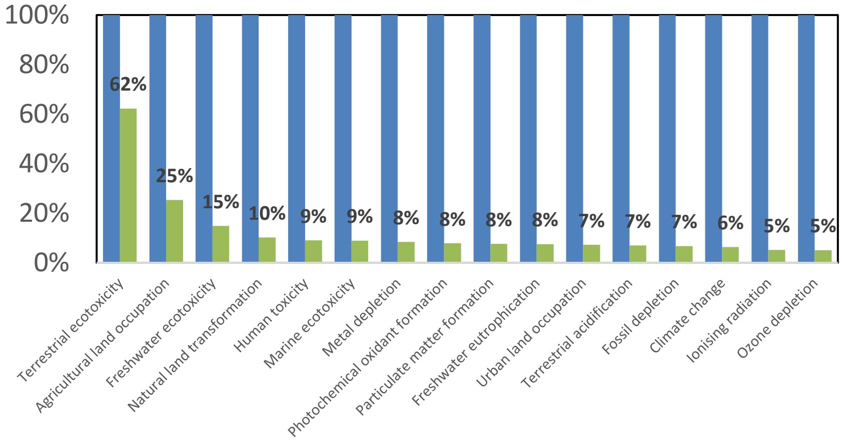
The production of daily life products such as food, feed, chemicals and pharmaceuticals involves large amounts of raw materials and energy (usually non-renewable) and generates waste with a negative impact on the environment. In this context, the research of new strategy and valid tools to reduce the overall impact of an industrial process seems to be essential. As matter of fact, industries are thus looking for alternative and sustainable technologies, able to reduce the amount of energy and water used and to minimize the fossil dependence. All actions aimed to enhance the greenness grade of the final desired products. Business model innovation and design, combine tools, methods and concepts such as creativity techniques, value network mapping, life-cycle assessment, and product-service systems. In this study, a Life Cycle Assessment (LCA) methodology was applied to support business model innovation and design sustainable strategies compared to the most consolidated alternative in the sector of detergents. An innovative product, a super concentrate pre-measured packets for floor cleaning and for daily maintenance of floors is counterposed to a traditional detergent and a LCA analysis is carried out to evaluate the environmental benefits as a consequence of its utilization. The results show that the smart product implies a resources usage (both renewable and non-renewable) lower than -92% if compared those used by the traditional product. In addition, a midpoint analysis carried out for the eighteen impact categories of the ReCiPe method shows a reduction trend from -38% up to -95% for the concentrated product (green in the figure below).



Non destructive characterization study of Picenes glass beads

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Studies carried out in the last decades defined that two main ethnic groups existed along the Italian Adriatic coast from the beginning of the Iron Age to the Romans conquest: Jalepigi and Sabelli, which were in turn divided into various tribes, including Picenes, living in the current coastal area of the Marche and of the northern Abruzzo regions between the 1st millennium B.C. and the 3rd century A.D.

The excavations of two Picene necropolises in Novilara (9th-7th century B.C, PU) and Matelica (9th-6th century B.C., MC) uncovered various grave goods including many colored glass, shell and bone-based beads.

A non-invasive characterization these beads has been performed by means of analytical techniques such as Reflectance and Raman spectroscopy and X-Ray diffraction.

Raman spectroscopy resulted particularly useful in the characterization of shell and bone based beads, displaying the typical spectra of calcite and Ca-phosphate, respectively, parallel reflectance spectroscopy gave information about the use of different chromophores in blue glass beads: as expected spectra of the darker samples contain the typical features of tetrahedral Co^{2+} ions, while data obtained from the two light blue beads available, coming from the Matelica necropolis, showed no traces of this metal but only the spectral profile deriving from the presence of Cu^{2+} ions. As known from literature, turquoise glass was commonly used during the Bronze Age, while cobalt started to be employed as a colorant during the Final Bronze Age in association with copper and then became the dominant metal to obtain dark hues due to its high colouring efficiency (1,2,3,4,5).

Both Reflectance and Raman Spectroscopy allowed the identification of hematite as the colouring agent of the only red bead available, coming from the Novilara necropolis. This is a very peculiar result, since no literature data have been reported so far, to the best of our knowledge, about the use of hematite in glassy beads dated to the Iron Age.

White and yellow samples were mainly studied by XRD: in both cases the use of traditional opacifiers such as Ca and Pb antimonates was demonstrated. Yellow samples in particular displayed the presence of lead pyroantimonate ($Pb_2Sb_2O_7$), whose diffraction peaks could be well distinguished over the broad glass structure; on the contrary, the collection of patterns from white samples, exhibiting a black surface decorative coating, gave results more difficult to be interpreted.

References

1. J. Henderson, Electron Probe Microanalysis of Mixed-Alkali Glasses, *Archaeometry,* 30 (1988) 77-91; **2.**Y. Billaud, B. Gratuze,. Les perles en verre et en faïence de la Protohistoire française. In: *Matériaux, productions, circulation, du Néolithique à l'Âge du Bronze,* Paris, 2002, pp.193-212; **3.** B. Gratuze, M. Picon, Utilisation par l'industrie verrière des sels d'aluns des oasis égyptiennes au début du premier millénaire avant notre ére. In *L'alun de Méditerranée,* Naples, 2006, pp. 269–276; **4.** A. J. Shortland, H.Schroeder, Analysis of first millennium BC Glass vessels and beads from the Pichvnari Necropolis, Georgia, *Archaeometry,* 51(2009), 947-965; **5.** S. Panighello, E. F. Orsega, J. T. van Elteren, V. S. Šelih, Analysis of polychrome iron age glass vessels from Mediterranean I, II and III groups by LA-ICP-MS, *Journal of Archaeological Science,* 39 (2012), 2945-2955.

Chemical investigations of bitumen from Neolithic flint flakes recovered from archaeological excavations in Central-Southern Italy

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The accessibility and distinctive chemical-physical properties of bitumen have made it one of the materials of choice since antiquity as adhesives, hydro-repellents, coating and sealing agents for the production of stone tools, ceramic vessels, ornaments and works of art. Bitumen belongs to the class of fossil materials formed by the evaporation of volatile components, polymerization and maturation reactions over geological timescale. This kind of fossil substance is particularly present in the Middle-Eastern region. Nevertheless, deposits of bitumen of different geological eras can be also found all over Europe. From a chemical point of view, bituminous materials are really complex mixtures of long-chain acyclic hydrocarbons, cyclic compounds such as hopanes and steranes, and aromatics. The composition of the bitumen varies depending on the area of origin, this means that the chemical characterisation of an archaeological bitumen can allow us not only to draw hypotheses on the possible function of tools/objects from which the bitumen is sampled, but also to obtain information on the geographical origin of the bitumen.

This paper will present the most important results regarding the characterization of bituminous residues sampled from Neolithic flint flakes recovered from archaeological excavations in Abruzzo and Puglia (Italy). Because of the chemical complexity of such organic substances, analytical procedures based on gas chromatography and mass spectrometry (GC/MS, Py-GC/MS) and on thermal analysis (TGA also coupled with IR detector, EGA-MS) have been chosen. The analytical protocol has been optimized and primarily tested in the study of bituminous materials (used as reference materials) from rocks and sediments of Central-Southern Italy, and subsequently used to characterize the archaeological bituminous materials recovered from the Neolithic stone tools.

Oli siccativi: approccio multi-analitico per l'identificazione di finger-print su campioni non trattati

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L'obiettivo di questa ricerca è stata l'identificazione, mediante analisi termica e termogravimetrica (DTA/TG) accoppiata alla gas cromatografia e spettrometria di massa (GC-MS) di *finger-print* caratteristici degli oli siccativi. Attualmente il riconoscimento di questo genere di leganti avviene basandosi sul rapporto tra le quantità di acido palmitico e acido stearico presenti (Tabella 1) (1) e le analisi hanno di norma necessità di un pretrattamento iniziale del campione (2,3).

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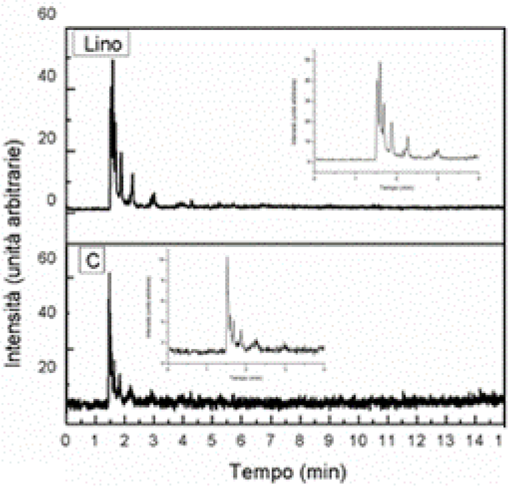
	OLIO DI LINO	OLIO DI NOCE	OLIO DI PAPAVERO
P/S	1,1-2,4	2,3-3,6	3-7

Lo studio si è focalizzato sui principali oli siccativi di uso artistico: oli di lino, di noce e di papavero (4,5). Questi sono stati invecchiati artificialmente a 40°C in atmosfera di O_2 per un mese e quindi analizzati con le tecniche sopra citate. In particolare da 35° a 600°C con rateo di riscaldamento di 5°C/min in atmosfera di He (20 ml/min) con la contemporanea analisi dei gas evoluti. Sono state eseguite sia analisi con colonna mantenuta in isoterma, che corse cromatografiche in punti risultati particolarmente interessanti al fine di poter discernere in modo più accurato le molecole rilasciate dai campioni. Interessanti risultati si sono ottenuti investigando le specie rilasciate intorno a 400°C, identificando molecole riconducibili ai diversi oli. La metodica è quindi stata applicata su campioni derivanti da opere reali, un dipinto su tela (XIX secolo) e uno su tavola (XV secolo) riuscendo a discriminare non solo la componente organica derivante dagli oli (Figura 1) ma anche la componente "grassa" derivante dai leganti proteici. Per queste ragioni, la tecnica accoppiata DTA/TG – GC/MS potrebbe essere considerata una nuova metodologia nello studio e nella diagnostica dei Beni Culturali.



References
1. J.S Mills, *Gas Chromatographic Examination of Paint Media, Part 1. Fatty Acid Composition and Identification of Dried Oil Films*, Studies in Conservation, 11 (1966) p. 107; **2.** M. Lazzarini, O. Chiantore, *Drying and oxidative degradation of linseed oil*, Polymer Degradation and Stability, 65 (1999) p. 303-313, **3.** I. Bonaduce, A. Andreotti, *Py-GC/MS of organic paint binders*, Organic mass spectrometry in art and archaeology, 2009, p. 303-326;
4. A. Casoli et al, *Gas chromatographic-mass spectrometric approach to the problem of characterizing binding media in paintings*, Journal of chromatography A, 731 (1996) p. 237-246; **5.** A. Andreotti et al, *Characterisation of natural organic materials in paintings by GC-MS analytical procedures*, New Trends in Analytical, Environmental and Cultural Heritage Chemistry, (2008) p. 1-35.

Biodiesel from transesterification of waste vegetable oils by means of heterogeneous biocatalyst

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The traditional methods for biodiesel production include the use of alkaline catalysts, like potassium hydroxide and sodium hydroxide, since they are cheap, easy to handle, to transport and store, or solutions of sodium methoxide and potassium methoxide in methanol, which are preferred for continuous-flow processes.

However, alkaline catalysts involve high temperatures, undesired by-products formation and difficulties in glycerol recovering. The post-treatments required could thus affect the energy and environmental benefits of using biodiesel.

For these reasons, research aims at identifying alternative and innovative solutions, including enzymatic catalysis: enzymes operate at low temperatures, pressures and controlled pH, while maintaining low energy consumption and high selectivity.

In the present work, we verified the feasibility of producing biodiesel through the transesterification of waste vegetable oils using as catalyst a lipase (enzyme) obtained from Solid State Fermentation (SSF) of agro-food by-products. In order to ease the catalyst recovery at the end of the reaction, the lipase was adsorbed on two different types of waste glass: funnel glass from Cathode Ray Tube (CRT) (PbO=12-25% wt) and packaging glass from urban collection (PbO≈5%wt).

Waste glasses were firstly ground and sieved in order to obtain 180-300 µm particle size. Subsequently, they underwent a series of chemical treatments, which can be distinguished into surface cleaning by means of acidic and basic solutions (Treatment A and B) and silanization (C) using two different silanizing agents: chlorotrimethylsilane (shorter -CH_3 chain) and tributylchlorosilane (longer -CH_3 chain).

Lyophilized lipase (150 U/g) was dissolved in phosphate buffer (pH 7) in order to obtain a lipase solution with 2 U/ml. The enzyme was immobilized on the solid carriers by adsorption keeping the glass grains in contact with the lipase solution in the following conditions: 230 rpm, T=30°C, 22 hours. The transesterification reaction of waste vegetable oils was carried out by means of the heterogeneous catalyst (lipase adsorbed onto glass grains) using methanol as reagent and cyclohexane as solvent in the following conditions: 250 rpm, T=30°C, 24 hours. In order to calculate the reaction yield, nonadecanoic acid was added as standard. Methyl esters were detected by means of GC-MS analysis.

Results confirmed the feasibility of the process: methyl esters typical of biodiesel (Hexadecanoic acid, methyl ester and 9-Octadecenoic acid (Z)-, methyl ester) were detected in all the samples containing lipase adsorbed on packaging glass for urban collection. CRT glass was less performing as support for lipase, since two samples containing this kind of glass didn't give any transesterification products. The reason could be the high level of PbO of this glass (12-25% wt), but further analyses should be carried out in this regard.

Further investigations could concern: i) the use of higher lipase concentrations to increase the reactions yields (the current ones are <1%), ii) the use of alternative supports to glass (e.g. porous geopolymers); iii) LCA study of the process; iv) the use of methanol obtained from pyrolysis of cellulosic materials (pruning residues, dried legumes).

Application of laser technology in cleaning metal threads of ancient liturgical vestment (chasuble)

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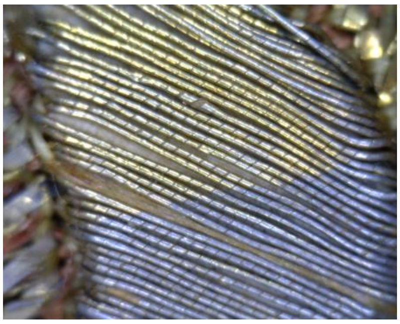
This paper focuses on the laser cleaning of metallic threads present as decoration on an ancient liturgical vestment using a Nd:YAG laser radiation in the visible region of the spectrum (532 nm). The chasuble, dating from early 18th century, belongs to the ancient textile collection of the Palatine Chapel in Palermo. This cleaning method, rarely used in the past on historical textiles, ensured a quick removal of the thick layer of oxidation and organic deposits present on the metal surface, providing the safety conditions for the artifact. The laser cleaning treatment revealed the ancient splendor of the chasuble and it was once again visible the richness and variety of decorative form, materials and techniques used for its production.

The (ICP–OES) analysis, carried out for the recognition of metal alloys, identified different composition for metallic yarn inserted on the perimeter area than those embroidered on the central area which have all similar composition. They are also applied three different kind of perimeter gallons in metallic yarns made on frame. On the chasuble there are a total of 11 different types of metal yarns, variables for construction technique, size, and surface appearance. The gold effect is obtained by applying a superficial gold layer on a silver alloy yarn.

The tests were carried out on different kind of thread, selecting small areas of 5 X 5 cm size. The average of the laser application time was 1 minute, while keeping a constant frequency of 10 Hz and changing the fluence in relation to the thickness of the oxidation layer.

The surface on which the laser runs has been previously moistened by applying a thin layer of water with a brush in order to contain the thermal spike, lowering the surface temperature. Humidification also facilitated the dirt removal due to the effect of the water vaporization. It was also used non-acidic small cardboard masks in order to protect the surface from the relapse of micro and nano-particulate redeposit that can attach the treated areas in case of prolonged irradiation (which would accelerate the reactivity) (1,2).



References
1. L. Nucci, R. Pini, A. Brunetto, *Kermes*, 2001, 42, 29; **2.** P. Belluzzo, S. Siano, G. Pieri, G. Lanterna, C. Innocenti, Kermes, 2007, 59, 67.

Protective effect of linseed oil varnish on archaeological wood treated with alum.

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The Viking Age wood artifacts recovered in the early 1900s from the Oseberg mound and treated with alum, are today highly degraded, a condition attributed to the effects of the alum-treatment and of the reactivity of alum and derived salts (1). Some of the artefacts from the Oseberg collection which were treated with alum were also coated by linseed oil. Although the linseed oil did not fully penetrate the wood in many cases, these artifacts appear to be in better physical condition than those not treated with linseed oil.

In order to assess the effect of the presence of linseed oil on wood preservation, alum treated wood coated with linseed oil was investigated. The fragment was sampled at different depths from the surface. Three analytical techniques, giving relevant information about the molecular composition and state of preservation of both archaeological wood and aged linseed oil, were adopted: gas chromatography coupled with mass spectrometry (GC-MS), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and high-performance liquid chromatography coupled to electrospray ionisation and quadrupole time-of-flight mass spectrometry (HPLC-ESI-Q-ToF).

Specifically, Py(HMDS)-GC/MS allowed to assess the state of preservation of the main wood components in the presence of linseed oil and the alum treatment, while GC-MS and HPLC-ESI-Q-ToF were used to perform the lipid characterization and to investigate the lipid degradation and oxidation processes.

The results showed that although the wood was highly depleted of carbohydrates (2), it was better preserved with respect to those artefacts not coated with linseed oil. Results from GC-MS and HPLC-ESI-Q-ToF together with those from Py-GC/MS suggested that the linseed oil played a mitigating role towards wood degradation. The behavior of the lipid material, more oxidized on the wood surface than at depth, suggested that selective oxidation of the oil over the wood components led to a better preservation of the material.

References
1. C.M.A. McQueen, D. Tamburini, J.J. Łucejko, S. Braovac, F. Gambineri, F. Modugno, M.P. Colombini and H. Kutzke, New insights into the degradation processes and influence of the conservation treatment in alum-treated wood from the Oseberg collection, Microchemical Journal, (2017) http://dx.doi.org/10.1016/j.microc.2017.01.010; **2.** S. Braovac, D. Tamburini, J.J. Łucejko, C. McQueen, H. Kutzke and M.P. Colombini, Chemical analyses of extremely degraded wood using analytical pyrolysis and inductively coupled plasma atomic emission spectroscopy, Microchemical Journal, 124, (2016) 368.

The weight of food on the environment: an emergy evaluation of Italians' diet

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Consumption of food represents 16% of Italian families' expenses. But what is the environmental cost of producing the food we consume? This can be estimated by emergy evaluation (1), accounting for the solar energy (directly and indirectly) required for the production of goods.

Since food component is showing an increasing relevance concerning its impacts, this study is aimed at highlighting the dietary habits of Italians from an emergy perspective. To this aim we have collected data to make an emergy database of food produced and consumed in Italy. In particular, we carried out emergy evaluations of the top 50 food products consumed by Italian citizens. For most of these products, since data were not available, ex novo emergy evaluations have been performed. Comparing the ideal food pyramid (2) with the one resulting from the calculation of the emergy per unit mass we have seen that the food that should be consumed more frequently (located at the bottom of the food pyramid), has a higher efficiency in the transformation from direct and indirect solar energy to food mass. The emergy per unit mass calculated in this research are then used to estimate the emergy flow necessary to support the current weekly Italian food diet. The optimum average dietary energy requirement suggested by the Italian Health Ministry is set at 14000 kcal per week. An ideal diet should also be as much as possible varied and nutritionally balanced, i.e. based on the consumption of food groups, as illustrated by the food pyramid as graphical representation of the "Mediterranean diet". A comparison between the current Italian diet and an ideal Mediterranean, vegetarian and carnivore diets has been then performed.

Results of this research have demonstrated that the emergy of diets can vary as a wide range of values and that the ideal Mediterranean diet seems to be a good tradeoff between low emergy requirements and diversity of food. In fact, in absolute terms, the vegetarian diet shows the lowest emergy per week (3.53×10^{13} sej), very close to the Mediterranean one (3.74×10^{13} sej). On the contrary the carnivore diet shows the highest emergy requirements (5.81×10^{13} sej), around 55% higher than the vegetarian diet. The current Italian diet shows a requirement 10% higher than the emergy flow with respect to the Mediterranean diet, although the composition of the current Italian diet, is moving away from the Mediterranean one.

This study shows the relevance of a proper education on food and diets both from the health and an environmental view point since about 20% of the overall emergy supporting an average Italian (expressed in sej yr^{-1} $person^{-1}$) is related to food provision (3).

References

1. Odum, H.T., 1996. Environmental Accounting: Emergy and Decision Making. Wiley, New York; **2.** USDA, 1992. The Food Guide Pyramid. Home and Garden Bull. No 252, 32 pp; **3.** Morandi F., Campbell D.E., Pulselli F.M., Bastianoni S., 2015. Emergy Evaluation of hierarchically nested systems: application to EU27, Italy and Tuscany and consequences for the meaning of emergy indicators. Ecological Modelling, 315, 12-27.

Effects of environmental parameters biomonitoring polycyclic aromatic hydrocarbons in the air by *Salix matsudana* leaves.

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Persistent organic pollutants (POPs) encompass many organic contaminant classes that show high persistence, susceptibility for long-range transport (LRT), and potential for biomagnification in food chains (1,2). Air is an efficient medium for the global dissemination of persistent organic pollutants (POPs). Epidemiological studies investigating the health risks related to air pollution suggest that ambient air pollution (including polycyclic aromatic hydrocarbons, PAHs) may be responsible for increased rates of diseases like lung cancer (3, 4). Air pollution is an important environmental problem that can result from both human and natural actions. To reduce pollution levels and minimize harmful effects on human health, it is necessary to improve air monitoring and provide useful information to the communities. Recently, biomonitoring methods using passive plant samplers may offer a practicable low cost alternative, especially in terms of high spatial resolution and time-averaged data series (5, 6). In this study, seasonal distribution characteristics of PAHs in *Salix matsudana* leaves covering its annual life cycle were carried out in order to evaluate plant leaf response sensitivity on air pollution. *Salix matsudana* leaves were collected throughout different development phases of plant leaf inclusive of bud break to fallen leaves, covering from spring (May) to autumn (November). Simultaneously, particle and gas samples were collected using a high volume air sampler. Seven different PAHs were determined from three types of samples. The leaf area and lipid content changed from season to season: both parameters increased rapidly during the spring season, maintained a stable state in summer season, while lipid content dramatically decreased in autumn season. Except spring season, total PAHs showed similar seasonal trends between plant leaves and air samples, with correlation coefficients equal to 0.74 and 0.56 in summer and autumn season, respectively. In this work, it has been demonstrated that climate changes, such as rainfall and air mass movement, influence the daily concentrations of PAHs in leaf. Furthermore, PAH composition profile in leaves and air phase have been correlated by principal component analysis.

References

1. Hung, H., Macleod, M., Guardans, R., Scheringer, M., Barra, R., Harner, T., Zhang, G., 2013. Atmos. Environ. 80, (6), 591–598; **2.** Tom, H., Farrar, N.J., Mahiba, S., Jones, K.C., Gobas, F.A.P.C., 2003. Environ. Sci. Technol. 37, (11), 2486–2493; **3.** Pavel, C., Jana, K., Tomás, B., Zuzana, F., Jirí, K., Ivan, H., 2006. Environ. Pollut. 144, (2), 406–413; **4.** Parodi, S., Stagnaro, E., Casella, C., Puppo, A., Daminelli, E., Fontana, V., Valerio, F., Vercelli, M., 2005. Lung Cancer 47, (2), 155–164; **5.** Mi, T., She-Jun, C., Jing, W., Yong, L., Xiao-Jun, L., Bi-Xian, M., 2012. Environ. Sci. Technol. 46, (5), 2708–2714; **6.** Tarricone, K., Wagner, G., Klein, R., 2015. Ecol. Indic. 57, 341–359.

Development of a qualitative and quantitative analytical method for the characterization of mixtures of free fatty acids and metal soaps in paint samples

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Until the 18th century, the paint production was at the basis of the activities in artists' ateliers: pure raw materials were purchased and then the paints were prepared according to traditional and sometimes secret recipes. From the XX century onwards, as a results of the scientific and technological industrial advancements, artists' oil paints were increasingly produced on an industrial scale: respect to the traditional oil paint media, the ingredients of industrial paints were modified to produce different working proprieties such as viscosity, drying rate, and color. In the modern oil formulations metal soap are commonly introduced as surfactant additives to facilitate the dispersion of pigments into the medium: dispersing agents were added to paints since the 19th century, and aluminum and zinc stearates were patented as dispersion agents and widely used after 1920. Metal soaps have the tendency to aggregate, and they may lead to the formation of inclusions, which can sometimes form lumps or protrusions on the paint surface, or can migrate from a paint layer to an adjacent one. Moreover, the presence of metal soap, can lead to an alteration of the speed of the hydrolysis processes involving the polymer network, leading to a deterioration of painting and painted surfaces (1).

The quantification of fatty acid metal carboxylates is often difficult, especially in mixture with free fatty acids. Different analytical methods based on gas chromatography/mass spectrometry (GC/MS) and infrared spectroscopy (FTIR) have been applied for the evaluation of metal carboxylates, but commonly their amount and type is determined together with free fatty acids or after specific sample pretreatment procedures.

In this work, we present the application of a new qualitative and quantitative analytical approach based on the use of GC/MS for the complete characterization of mixtures of free fatty acids and metal carboxylates in paint samples (2).

In this new method, we combined two silylation reactions directly on the same paint sample in order to derivatize in two different analytical steps the carboxylic and the carboxylate groups.

In the first step 1,1,1,3,3,3-hexamethyldisilazane (HMDS), that did not show affinity with the metal soap carboxylate groups, was applied for the derivatization of the fatty acids, while N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was applied for the silylation of the metal carboxylate. The combination of this two derivatization procedures on the same paint sample allowed us to discriminate and quantify free fatty acids and metal carboxylates directly on the paint sample without any sample pretreatment.

This new analytical approach was successfully applied to characterize the chemical composition of paint samples.

References

1. K.J. van den Berg, Issues in Contemporary Oil Paint, Springer 2014; **2.** J. La Nasa, F. Modugno, A. Lluveras-Tenorio, I. Bonaduce, Development of a GC/MS method for the qualitative and quantitative analysis of mixtures of free fatty acids and metal soaps, Journal of Chromatography A, submitted.

Early Medieval Globular Amphorae from Torcello: Microscopy, Porosity and Chemical Analyses for the Study of Production Techniques

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This work aims to study the production techniques, such as firing temperature, on selected globular amphorae fragments uncovered during the 2012-13 archaeological excavation at Torcello, Venice. Particle packing, microstructure, porosity and morphology, as well as chemical-mineralogical composition of ceramic matrix, are correlated with native material composition and firing temperature (1,2). Considering these physical and chemical properties, the samples were investigated and the results obtained through Mercury Intrusion Porosimetry (MIP), Scanning Electron Microscope (SEM-EDX) and Fourier-Transform Infrared Spectroscopy (FT-IR) were compared.

We considered some selected fragments of Early Medieval Globular amphorae, dating from the 7th to the 10th century, excavated in the 2012-13 archaeological excavation in Torcello (one of the first settled island on the northern Venetian lagoon) (3).

The samples are rich in SiO_2 and Al_2O_3 with varying amounts of CaO, Fe_2O_3, MgO, K_2O and TiO_2. Calcite was detected in some sherds, indicating Ca-rich raw materials and low-firing temperature. The presence of carbonate-rich clay promotes high porosity over 600°C, as a result of CO_2 exhaust. Decomposition of calcite begins at T>650°C and the phase disappears at T>850-900°C. Hence, the presence of calcite in ceramic fired at T>900°C could be due to a secondary calcite, formed from a reaction between CaO and silicates (4). Porosity results obtained by MIP allowed an estimation of the open porosity and pore size distribution of meso and macropores. Furthermore, a comparison between the MIP results and those obtained by digital image analyses of SEM micro-photographs, was evaluated.

The combined use of chemical and physical techniques has outlined the information about the raw materials and the technological–productive aspect. We have collected new data in order to estimate the firing temperature of the ceramic samples.

References
1. M.P. Riccardi, B. Messiga, P. Duminuco, An approach to the dynamics of clay firing, Applied Clay Science 15, 393-404, 1999; **2.** G. Dal Sasso, L. Maritan, S. Salvatori, et.al., Discriminating pottery production by image analysis: a case study of Mesolithic and Neolithic pottery from Al Khiday (Khartoum, Sudan), Journal of Archaeological Science 46, 125-143, 2014; **3.** D. Calaon, E. Zendri, G. Biscontin, Torcello Excavated. A shared Heritage, Regione Veneto, vol. 2, 2014; **4.** K. Traorè, G.V. Ouèdraogo, P. Blanchart, et.al., Influence of calcite on the microstructure and mechanical properties of pottery ceramics obtained from a kaolinite-rich clay from Burkina Faso, Journal of the European Ceramic Society 27, 1677–1681, 2007.

Monoalkyl glyceryl ethers production in the presence of homogeneous and heterogeneous acid catalysts

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Monoalkyl glyceryl ethers (MAGEs) are valuable chemical compounds with different industrial applications, such as the formulation of additives (for fuels, lubricants, printing inks etc.), detergents, polymers, pharmaceuticals, antiseptic and antimicrobial creams. (1)

In this work, we report the synthesis of MAGEs by ring opening reaction of glycidol (2,3-epoxy-1-propanol) with alcohols in in the presence of both homogenous and heterogeneous acid catalysts.

The use of glycidol as starting material to produce such valuable chemicals seems to be very promising since it can be obtained through the conversion of 2-chloro-1,3-propanediol, a by-product in the epichlorohydrin production plant. (2)

Recently we have studied the etherification of glycidol with different alcohols (ethanol, methanol, 2-propanol, 1-butanol, 1-pentanol, 1-octanol, and benzyl alcohol) in the presence of Lewis acid based catalyst such as metal chlorides and triflates. (3)

The experiments were carried out at 80°C and alcohol/glycidol moles ratio of 9 using different alcohols (methanol, ethanol, 2-propanol, tert-butanol, 1-butanol, 1-pentanol, 1-ottanol and benzyl alcohol) as nucleophiles. Results show that $Bi(OTf)_3$, $Al(OTf)_3$, $Fe(OTf)_3$ are able to catalyze the reaction of glycidol with alcohols at 80°C in 1 h using a catalyst loading of 0.01 % in moles. In the light of these results we have synthesized the corresponding heterogeneous catalysts using mesoporous silica as support.

The heterogeneous triflates have shown the same activities of the corresponding homogeneous one in terms of conversion (95%, 75% and 70% in 1 h respectively for Al, Bi and Fe) and selectivity (>90%) to MAGEs. However, a loss of catalytic activity was observed during the first reuse. Moreover, we have tested other heterogeneous catalyst such as sulfonated mesoporous silica, sulfonated activated charcoal and functionalized polymeric resins. The best results were obtained by using Nafion NR50, a perfluorinated ion-exchange polymer. This catalyst was stable under the investigated experimental conditions also after four subsequent reaction cycles.

References
1. Sutter, M.; Silva, E. D.; Duguet, N.; Raoul, Y.; Métay, E.; Lemaire, M. *Chem. Rev.* 2015, *115*, 8609-8651; **2.** Cespi, D.; Cucciniello, R.; Ricciardi, M.; Capacchione, C.; Vassura, I.; Passarini, F., Proto, A. *Green Chem.* 2016, *18*, 4559-4570; **3.** Cucciniello, R.; Ricciardi, M.; Vitiello, R.; Di Serio, M.; Proto, A., Capacchione, C.; *ChemSusChem* 2016, 9, 3272–3275.

Nano-Cathedral project: experimental results from the evaluation of the performance protective treatments and insight into their interaction with stone materials

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The EU-funded Nano-Cathedral project is about the design, laboratory evaluation and on-site testing of innovative nanomaterials for the conservation of historic stone architecture. The nanomaterials are to be applied for *consolidation* or *protection* purposes on a selection of six lithotypes of five different European cathedrals and of a monument of contemporary architecture. The ultimate goals are first and foremost to build up a systematic knowledge of the characteristics of nano-structured products that are most relevant to their effectiveness in the treatment of different natural stones and also to promote an integrated European-wide approach to the use of innovative materials in the field of cultural heritage conservation (1).

Our research activity in the frame of the project is currently aimed at:

- implementing a laboratory protocol for the evaluation of the performance protective treatments on the selected lithotypes and their combined response towards environmental exposure;
- investigating the interaction between nanomaterials and lithotypes.

The protective treatments under study fall into three different categories: *photocatalytic* treatments, *biocidal* treatments and a *purely water-repellent* nanopolymer.

Concerning the first aim of the research, a characterization of about 60 stone specimens was carried out for each of the six lithotypes *before* and *after* the application of the treatments, including measurements of capillary water absorption, water vapour permeability, static contact angle and colour change. As regards the characterization of photocatalytic activity, we have worked so far on an optimization of the Rhodamine discolouration test on stone specimens and planned to carry out further tests on the treatments in their liquid form. The data obtained so far allowed us to fully characterize the performance of six nanomaterials, highlighting very clearly the differences among them if applied on different lithotypes. Regarding the interaction between nanomaterials and lithotypes, we are obtaining promising results from an electrokinetic technique, the streaming potential analysis, which provides an insight into the modification of stone properties after the application of the treatments and the chemical affinity between treatments and lithotypes. As future activity, all treated specimens will undergo an artificial ageing procedure in order to predict their response towards environmental exposure.

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Reference

1. A. Lazzeri, M.-B. Coltelli, V. Castelvetro, S. Bianchi, O. Chiantore, M. Lezzerini, L. Niccolai, J. Weber, A. Rohatsch, F. Gherardi, L. Toniolo, European Project "NANO-CATHEDRAL: Nanomaterials for conservation of European architectural heritage developed by research on characteristic lithotypes, in Hughes, J., & Howind, T. (Eds.) (2016). Science and Art: A Future for Stone: Proceedings of the 13th International Congress on the Deterioration and Conservation of Stone, Volume 1. Paisley: University of the West of Scotland, pp. 847-854.

Ageing of mono-azo and β-naphthol red and yellow synthetic organic pigments in painting matrices and textiles

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In the second half of the 19th century, chemical synthesis established and quickly developed. The new synthetic organic pigments (SOPs) quickly replaced the traditional natural organic dyes (extracted by vegetal and animal sources) due to their cheapness, great range of bright nuances and wide availability. Hundreds of these SOPs have been used for a variety of applications and exploited in the artistic field. The introduction of ready-to-use tube colours radically changed the way in which artists approached painting and SOPs have, since then, become the most important group of pigments used in modern art (1). Among the several classes of synthesized SOPs, β-naphthols, belonging to the class of azo pigments and obtained by coupling reactions, were considered the first successfully used in textile dyeing and printing (2). Nevertheless, the fastness proprieties of most of the azo dyes were not tested sufficiently before their introduction on the market and the absence of information about the miscellaneous additives used by paint manufactures in the commercial formulations resulted in a general lack of knowledge of the chemistry of these species in modern artworks.

This work aims to study the degradation and fading processes due to ageing and oxidation of some β-naphthol and mono-azo SOPs, not much investigated until now, such as the orange and red pigments Pigment Orange 5 (PO5), Pigment Red 3 (PR3), Pigment Red 53 (PR53), Pigment Red 49:2 (PR49:2), Fast Red AV and the yellow pigments and dyes Naphtol Yellow S (NY), Martius Yellow (MY) and Pigment Yellow 1 (PY1). Methods based on High Pressure Liquid Chromatography coupled with Diode-Array, Fluorescence or Mass Spectrometric Detectors (HPLC-DAD-FD-MS) were developed and optimized considering the chemical features of these SOPs and exploiting their high fluorescence. A novel C18 solid silica core column (Poroshell 120 EC-C18) was tested for the optimization of the analytical methods. The target compounds were studied both as pigments (e.g. casted on glass slides dispersed in isopropanol, or in more complex media constituted by linseed oil and white inorganic fillers) and as dyes on wool yarns. These mock-ups were naturally or artificially aged in order to study the degradation products and in some cases also the relative kinetics. The results allowed us to understand if and how the matrix influences SOPs' degradation rate and the formation of the different intermediates and end-products. Moreover, the differences between the degradation profiles of the different pigments belonging to the same class (β-naphthol) or to a different one (mono-azo) have been evaluated and some hypotheses about the degradation pathways have been formulated.

The analyses carried out so far provide preliminary results that will be further investigated analyzing extremely aged mock-ups and historical paint samples. Nevertheless, this work adds a missing piece of information to the little-known topic of the degradation of modern pigments. The final results of this study will eventually help restorers and curators to prevent or slow down deterioration processes and choose the most suitable procedures for preserving artworks.

References

1. I. Fyfe, Arts & Reviews: Modern World, Modern Art, Bluesci-Cambridge University Magazine,Vol. 19, p. 26-27, 2010; **2.** J. Oakes, Photofading of textiles dyes, Review of progress in Coloration and Related Topics, Vol. 31, 1, p. 21-28, 2001.

Orcein dyes and its synthetic alterego, the mauveine dyes: a threshold of a complete change

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Orchil dyes is one of the most fascinating dye in the art history. Considered as the "first" synthetic dye in the history, due to the treatment that the lichen should have been subjected to, in order to obtain the chromophores, it has been widespread used during the centuries, even if its detection in artworks is strongly compromised by its low photo-stability (1,2). As happened for other natural dyes, the discover of reaction for producing synthetic dye has led to their replacement with the synthetic alteregos. Furthermore, the mauveine, the real first synthetic dye in history, can be easily considered the alterego of orchil, due to a similar violet issue given to the yarns. Obviously, it is not easy to understand how much time the textile dye industry employed to spread in economic and social portrait of 20th century. For this reason, the *abito da passeggio* of Donna Concetta Tomasi di Lampedusa can be considered a precious historical proof, which can furnish several information about this matter. The multi-analytical approach applied to the study of dyes employed for the historical dress started from SERS on fiber analyses, which allowed hypothesizing the simultaneous presence of orcein and mauveine dyes (fig. 1). Thus, it has been chosen a selective extraction protocol for both dyes, followed by mass spectrometric analyses. In particular, the application of the new mild extraction technique, suitable for natural dyes, (3) allowed confirming the presence of orcein, albeit in a small amount. Furthermore, MALDI-ToF and HPLC-MS (fig.2) analyses confirm that it was used simultaneously with its synthetic alter ego, the mauveine, testifying its widespread diffusion in all over the Europe in only ten years, ready to completely replace the natural dye.

In particular, the identification of mauveine derivatives and their relative proportions can give additional important information, for what concerns the preparation of mauveine dyes and can be considered diagnostic for the synthetic recipes followed by the dyes industries in that period (4).

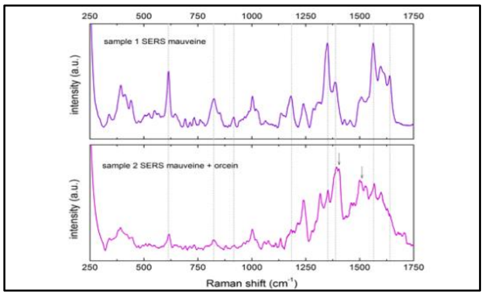

Fig. 1. SERS on fiber spectra performed on sample from the dress.

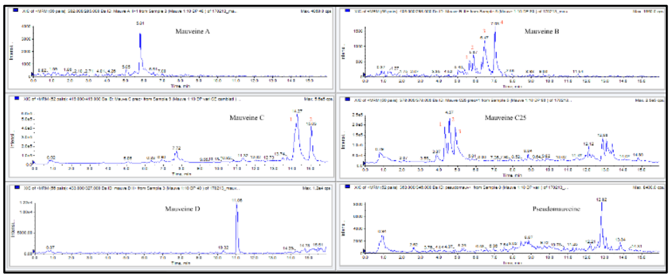

Fig 2. HPLC-MS of mauveine extract from the dyed yarns.

References

1. D. Cardon, Le Monde des Teintures Naturelles, Edition Bèlin, Paris, 2014; **2.** F. Rosi F., C. Clementi, M. Paolantoni, A. Romani, R. Pellegrino, B. G. Brunetti, W. Nowik, C. Miliani, Journal of Raman Spectroscopy, 44 (10), 2013, 1451-1453; **3.** L. Lombardi, I. Serafini, M. Guiso, F. Sciubba, A. Bianco, Microchemical Journal 126, 2016, 373–380; **4.** M. Conceiçao Oliveira, A. Dias, P. Douglas, J. S. Seixas de Melo, Chemistry - A European Journal, 20, 2014, 1808 – 1812.

Nuovo metodo per la pulitura di affreschi da sali solubili

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I dipinti murali rappresentano un inestimabile valore del patrimonio artistico mondiale, in quanto sono testimonianza di una tecnica molto antica. Essendo strettamente legate al supporto murario le pitture parietali risentono delle problematiche del supporto, come movimenti che generano crepe, infiltrazioni e risalita capillare dal terreno. Quest'ultimo problema, legato alla risalita capillare, può dare origine ad un ulteriore fenomeno di degrado: la manifestazione di efflorescenze saline sulla superficie delle pitture e all'interno del paramento murario.

Questo studio è incentrato su una nuova tecnica per la rimozione di sali solubili da affreschi e materiali porosi e la sua comparazione con le metodiche ad impacco note nel campo del restauro. La tecnica innovativa, basata sul brevetto dell'Università degli Studi di Genova (1) ha portato alla rimozione, su campioni opportunamente trattati, del 100% di sali in 60 minuti, mentre gli impacchi di polpa di cellulosa hanno rimosso il 20% in 120 ore. Per questo studio sono state utilizzate due specie saline note: NaCl e Na_2SO_4. Quest'ultimo è molto dannoso per i manufatti porosi a causa della pressione di idratazione e quella cristallizzazione a cui è soggetto (2,3). La fase di idratazione genera un forte aumento di volume (circa 314%) e il passaggio da fase anidra (detta thenardite) a fase decaidrata (4). Inoltre le condizioni climatiche come T e RH sono i principali fattori che innescano questo continuo meccanismo di cambiamento di fase; i materiali porosi soggetti a ripetuti cicli sono destinati a essere irrimediabilmente distrutti.

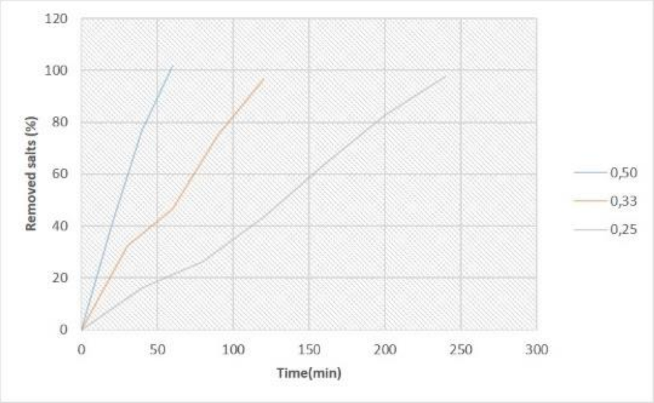

Fig.1. Rimozione di sali con differenti velocità di aspirazione.

Il grafico mostra come una portata di flusso di 0.50 m^3/min permetta di rimuove totalmente i sali in 60 minuti. La comparazione con i metodi ad impacco ha dimostrato che la nuova metodologia può essere utile per l'estrazione dei sali solubili dai supporti porosi e le due tecniche possono essere impiegate insieme.

References

1. G. Torrielli, L. Gaggero, M. Ferretti, "Apparatus and method for treating porous materials" PCT/IB2015/055129 (2015); **2.** R.J. Flatt, G.W. Scherer "Hydration and crystallization pressure of sodium sulfate: a critical review", P.B. Vandiver, M. Gordway, J.L. Mass (Eds.), Proceedings of Materials Research Society, 712, Materials Issues in Art and Archeology VI, Materials Res. Soc., Warrendale, PA 2002; 29–34. **3.** D. Benavente, M.A. Garcìa del Cura, R. Fort, S. Ordonez, "Thermodynamic modelling of changes induced by salt pressure crystallisation in porous media of stone", J. Cryst. Growth 1999; 204: 168-78. 4. N. Tsui, R.J. Flatt, G.W. Scherer, "Crystallization damage by sodium sulfate", J. Cult. Herit. 2003; 4: 109–115.

Study of calcium alkoxides as new solution for the consolidation of decayed limestone

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Limestone with different porosity are extensively used as a sculptural and architectural stone in artistic-architectural field. However, the combined action of several physical, chemical and biological factors, causes the weathering of stone leading to loss of surface and in-depth cohesion (1,2,3).

A novel consolidating product, calcium ethoxide, has been recently proposed during the European NANOMATCH project for the treatment of carbonate stones (4). In fact, this compound, dissolved in an organic solvent, reacts in presence of humidity and CO_2 to give in situ $CaCO_3$ and alcohols, leading to the filling of micro-fissures and reconsolidation of decayed stone (5). The carbonation process can follow two different reaction pathways: insertion of CO_2 molecule between Ca-O bond or insertion of H_2O molecule. The purpose of this research is the evaluation of carbonation process pathways of calcium ethoxide diluted in different organic solvent and the study of the consolidation effect of these new products on limestone widely employed within Italian Cultural Heritage, compared with a reference product.

Preliminary results regarding: variation of porosity (MIP), changing in mechanical and physical characteristics – drilling resistance measurement, ultrasound velocity, permeability test - and observation of treated surface – scanning electron microscopy - are here reported and discussed.

References

1. S. W. U. Massey, "The effects of ozone and NOx on the deterioration of calcareous stone," vol. 227, pp. 109–121, 1999; **2.** T. Warscheid and J. Braams, "Biodeterioration of stone: a review," vol. 46, pp. 343–368, 2000; **3.** E. Charola, A., "Salts in the deterioration of porous materials: an overview," *jAIC*, vol. 39, pp. 327–343, 2000; **4.** I. Natali, M. L. Saladino, F. Andriulo, D. Chillura Martino, E. Caponetti, E. Carretti, and L. Dei, "Consolidation and protection by nanolime: Recent advances for the conservation of the graffiti, Carceri dello Steri Palermo and of the 18th century lunettes, SS. Giuda e Simone Cloister, Corniola (Empoli)," *J. Cult. Herit.*, vol. 15, no. 2, pp. 151–158, 2014; **5.** P. Tomasin, F. Ossola, P. Tomasin, C. De Zorzi, and N. El Habra, "New Calcium Alkoxides for Consolidation of Carbonate Rocks . Influence of Precursors ' Characteristics on Morphology , Crystalline Phase and Consolidation Effects New calcium alkoxides for consolidation of carbonate rocks . Influence of," no. October 2015, 2012.

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	ABC PO37
Favero Gabriele	ABC/ANA/FIS OR05
Federici Ermanno	ABC OR03
Feltracco Matteo	ABC/ANA OR03
Fermo Paola	ABC OR21
Ferrari Anna Maria*	ABC OR05
Ferrari Pamela*	ABC/ANA/FIS OR02
Ferrero Luca	ABC OR27
	ABC/ANA OR05
	ABC/ANA OR07
Ferrero Luca*	ABC OR06
Ferretti Maurizio	ABC OR10
	ABC PO12
	ABC PO26
	ABC PO38
Ferretti Maurizio*	ABC PO16
Fico Daniela	ABC/ANA/FIS OR08
Fioravanti Marco	ABC PO22
Forti Luca	ABC PO27
Fossati Fabio	ABC PO12
	ABC PO38
Franzetti Andrea	ABC OR03
Frizzi Tommaso	ABC OR28
Fullana Andres	ABC PO06
Gabrieli Jacopo	ABC OR04
Galassi Maria Clelia	ABC PO26
Galeotti Monica	ABC OR26
Galimberti Cristoforo	ABC PO35

Pozzi Andrea	ABC PO05
Prati Silvia	ABC OR28
	ABC/ANA/FIS KN01
	ABC OR26
Profumo Antonella	ABC OR10
	ABC PO12
Proto Antonio	ABC KN01
	ABC OR12
	ABC OR23
	ABC PO23
	ABC PO34
	ABC/ANA KN03
	ABC/ANA OR07
Pulselli Federico Maria*	ABC PO30
Pulselli Federico Maria	ABC PO21
Pulselli Riccardo M.	ABC PO04
Quagliani Valeria	ABC PO24
Quinto Maurizio*	ABC PO31
Rabbolini Alfiero	ABC OR25
Raffo Simona	ABC OR14
Raffo Simona*	ABC OR27
Ribechini Erika	ABC OR22
	ABC PO20
	ABC PO36
Ribechini Erika*	ABC PO25
	ABC PO32
	ABC/ANA/FIS KN02
Ricci Giulia*	ABC PO33
Ricciardi Maria*	ABC PO34
Ridi Francesca	ABC PO22
Righetti Pier Giorgio	ABC/ANA/FIS OR07
Ritter Christopher	ABC PO11
Rivoira Luca	ABC PO09
Rivoira Luca*	ABC/ANA OR02
Rizzi Cristiana	ABC/ANA OR07
Robbiola Luc	ABC OR19
Robotti Elisa	ABC/ANA/FIS OR07
Roos Per	ABC OR07
Rosa Roberto	ABC OR05
Rosselli Annalisa	ABC OR09
Rossi Antonella	ABC/ANA/FIS OR09
Rossi Federico	ABC OR12
	ABC PO19
Rossini Paolo	ABC PO23
Rostagno Chiara	ABC/ANA OR07
Roveri Marco*	ABC PO35
Roviello Valentina*	ABC OR07
Ruberti Daniela	ABC OR07
Ruffolo Silvio Antonio	ABC OR21
Sabatini Francesca*	ABC PO36
Salanti Anika	ABC/ANA/FIS OR10
Salis Annalisa	ABC PO10
Salvini Antonella	ABC PO22
Samorì Chiara	ABC OR26
Santini Monia	ABC/ANA KN01
Scarchilli Claudio	ABC/ANA OR04
Sciubba Fabio	ABC OR20

	ABC OR29
	ABC PO37
Sciutto Giorgia *	ABC OR26
Sciutto Giorgia	ABC/ANA/FIS KN01
	ABC OR28
Sebastiani Bartolomeo	ABC OR03
	ABC OR17
Selvaggi Roberta	ABC OR03
	ABC OR17
Semenzin Elena	ABC PO01
Serafini Ilaria	ABC PO08
Serafini Ilaria*	ABC OR29
	ABC PO37
Sergi Manuel	ABC PO37
Servidio Alessandro	ABC OR09
Severi Mirko	ABC/ANA OR05
Severi Mirko*	ABC/ANA OR04
Shamsi Javad	ABC PO16
Siciliano Maria	ABC OR08
	ABC/ANA KN03
Siciliano Tiziana	ABC/ANA KN03
Siciliano Tiziana*	ABC OR08
Soggia Francesco	ABC OR17
Spada Lucia	ABC PO14
Spadaccino Giuseppina	ABC PO31
Speltini Andre	ABC OR10
	ABC PO12
Spepi Alessio	ABC PO25
Stenni Barbara	ABC/ANA OR04
Sturini Michela	ABC OR10
	ABC PO12
Tagliavini Emilio	ABC OR26
Takahama Satoshi	ABC OR21
Tamburini Diego	ABC OR22
	ABC/ANA/FIS OR10
Tempesti Paolo	ABC/ANA/FIS OR03
Terrasi Filippo	ABC OR07
Thomas Elizabeth R.	ABC/ANA OR04
Tinè Maria Rosaria	ABC PO25
Tomasin Patrizia	ABC PO39
Toniolo Lucia	ABC PO35
Torresan Silvia	ABC/ANA KN01
Torrielli Giulia*	ABC PO26
	ABC PO38
Tosi Alvise	ABC PO17
Tosi Cristian	ABC OR30
Tozzi Carlo	ABC PO25
Trabace Maddalena	ABC/ANA/FIS OR02
Tranvik Lars	ABC/ANA KN02
Traversi Rita	ABC PO11
	ABC/ANA OR04
	ABC/ANA OR05
Udisti Roberto	ABC PO11
	ABC/ANA OR04
Udisti Roberto*	ABC/ANA OR05
Valmacco Federico	ABC/ANA OR01
van Keulen Henk	ABC OR24
Vardè Massimiliano	ABC OR04

Vardè Massimiliano *	ABC OR09
Vassura Ivano	ABC OR14
	ABC OR27
	ABC OR30
	ABC PO15
	ABC PO34
Vespasiano Giovanni	ABC OR09
Vespignani Luca	ABC PO03
Vione Davide	ABC/ANA OR01
	ABC/ANA OR02
Vione Davide*	ABC/ANA KN02
Vitale Vito	ABC/ANA OR05
Vivani Riccardo	ABC OR17
Volanti Mirco*	ABC OR31
Volpi Ghirardini Annamaria	ABC PO01
Volpin Stefano	ABC/ANA/FIS OR06

Wei Ouyang	ABC/ANA KN01
Zangrando Roberta	ABC/ANA OR03
Zarrella Ilaria	ABC KN01
	ABC PO23
Zattini Giorgio	ABC OR30
Zborowska Magdalena	ABC OR22
Zelano Vincenzo	ABC/ANA OR06
Zendri Elisabetta	ABC PO33
	ABC PO39
Zhao Xiangai	ABC PO31
Zielinski Tymon	ABC PO11
Zirino Alberto	ABC/ANA KN01
Zoia Luca	ABC/ANA/FIS OR10
Zuena Martina	ABC PO33
Zuena Martina*	ABC PO39

DIVISIONE DI CHIMICA ANALITICA

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Delegato di Divisione

- Carlo Crescenzi, *Università degli Studi di Salerno*

Programma Scientifico

Divisione di Chimica Analitica

Lunedi' 11 Settembre 2017

	Sala Paestum A
Conferenza Plenaria: Chimica Analitica	
Chair: ***Aldo Roda***	
9.00 – 9.15	*Apertura Congresso della Divisione Chimica Analitica*
9.15 – 10.00	ANA-PL01: Luisa Torsi *Printable organic bioelectronics for bioanalytical detections at the physical limit: is this feasible?*
10.00 – 10.30	*Conferenza Vincitore del Premio Giovane Ricercatore* ANA-IN01: Susy Piovesana *Cutting-edge developments in shotgun proteomics, peptidomics and shotgun phosphoproteomics in real matrices*
10.30 – 11.00	Coffee Break
Sessione Parallela: ***Scienza delle Separazioni***	
Chair: ***Maria Careri***	
11.00 – 11.20	*Finalista premio Levi* ANA-IN02: Anna Laura Capriotti *A new magnetic graphitized carbon black TiO_2 composite for phosphopeptide selective enrichment in shotgun phosphoproteomics*
11.20 – 11.50	ANA-KN01: Sara Bogialli, Paolo Pastore, Luca Lucentini *High Resolution mass spectrometry: the re-evolution of the risk assessment and management*
11.50 – 12.10	ANA-OR01: Tonino Caruso *A validated SIM GC/MS method for the simultaneous determination of linear polyalkylsiloxanes OH-terminated in ctamethylcyclotetrasiloxane*
12.10 – 12.30	ANA-OR02: Giorgia La Barbera, Giulia Praticò, Göezde Gurdeniz, Maj Britt Schmidt Andersen, Lars Ove Dragsted *Identification of urinary biomarkers of meat and dairy products intake by means of UHPLC-QTOF/MS untargeted metabolic profiling*
12.30 – 12.50	ANA-OR03: Massimo Del Bubba, Lapo Renai, Claudia Ancillotti, Lorenzo Ciofi, Daniele Rossini, Leonardo Checchini, Maria Concetta Bruzzoniti, Serena Orlandini, Donatella Fibbi, Sandra Furlanetto *On-line SPE-LC-MS/MS analysis of wide-range polarity pharmaceutical compounds in aqueous matrices: problems and solutions*

Sala Olimpia	
Sessione Parallela ***Bioanalitica***	
Chair: ***Mara Mirasoli***	
11.00 – 11.30	ANA-KN02: Zangheri Martina, Mara Mirasoli, Laura Anfossi, Fabio Di Nardo, Cristina Giovannoli, Massimo Guardigli, Claudio Baggiani, Aldo Roda *Biosensors based on chemiluminescent-Lateral Flow Immunoassay: a powerful approach for integrated analytical platforms*
11.30 – 11.50	ANA-OR04: Nicola Marchetti, Caterina Bergantin, Annalisa Maietti, Luisa Pasti, Alberto Cavazzini *Insights into structure-bioaccessibility relationships of polyphenols in red chicory by HPLC-MS/MS*
11.50 – 12.10	ANA-OR05: Marcello Manfredi, Chiara Guglielmetti, Maria Mazza, Sonia Brusadore, Paolo Giuseppe Ubaldi, Luca Magnani, Stefano Gili, Emilio Marengo, Pier Luigi Acutis *Shotgun Proteomics for Detecting Seafood Fraud*
12.10 – 12.30	ANA-OR06: Matteo Crosera, Marcella Mauro, Elena Baracchini, Massimo Bovenzi, Francesca Larese Filon, Gianpiero Adami *In vitro meningeal permeation of $MnFe_2O_4$ Nanoparticles*
12.30 – 12.50	ANA-OR07: Camilla Montesano, Gabriele Vannutelli, Federico Fanti, Flaminia Vincenti, Roberta Curini, Adolfo Gregori, Anna Rita Togna, Matteo Marti, Isabella Canazza, Manuel Sergi *Identification of MT-45 metabolites: in silico prediction, in vitro incubation with rat hepatocytes and in vivo confirmation*
Sala Penelope	
Sessione Congiunta: ***Chimica Analitica - Elettrochimica - Gruppo Sensori***	
Chair: ***Aldo Roda***	
11.00 – 11.30	ANA/ELE/GS-KN01: Fabiana Arduini, Stefano Cinti, Giorgio Scordo, Renato Massoud, Danila Moscone, Giuseppe Palleschi *New Sustainable and cost-effective paper-based electrochemical (bio)sensors*
11.30 – 11.50	ANA/ELE/GS-OR01: Erika Scavetta, Federica Mariani, Isacco Gualandi, Domenica Tonelli, Marta Tessarolo, Beatrice Fraboni *All PEDOT:PSS electrochemical transistors as a platform for sensing*
11.50 – 12.10	ANA/ELE/GS-OR02: Alice Soldà, Marco Giorgio, Pier Giuseppe Pelicci, Nicholas Dale, Francesco Paolucci, Stefania Rapino *Development of enzyme-based microsensors for ex vivo analyses*
12.10 – 12.30	ANA/ELE/GS-OR03: Ornella Abollino, Andrea Ruo Redda, Francesca Durbiano, Eleonora Conca, Mery Malandrino, Agnese Giacomino *Potential and limitations of voltammetric measurements for the characterization of electrode surface*
12.30 – 12.50	ANA/ELE/GS-OR04: Laura Fabiani, Giulia Volpe, Elisabetta Delibato, Eleonora Pucci, Silvia Piermarini, Giuseppe Palleschi *Development of an electrochemical magneto-immunosensor for the detection of Campylobacter: a preliminary study*

Sala Athena	
"La Trasversalità della Chimica nei Beni Culturali" *Sessione Congiunta**: Chimica Analitica -Fisica - Chimica dell'Ambiente e dei Beni Culturali***	
Chair: ***Lucia Toniolo***	
9.00 – 9.25	ABC/ANA/FIS-KN01: Rocco Mazzeo, Stjin Legrand, Giorgia Sciutto, Silvia Prati, Emilio Catelli, Paolo Oliveri, Koen Janssens *Macro Mid-Infrared total reflection (MA-FTIR) mapping for the characterization of outdoor bronze surfaces*
9.25 – 9.40	ABC/ANA/FIS-OR01: Rachele Elisabetta Camerini *Silica-based composites for the consolidation of earthen materials*
9.40 – 9.55	ABC/ANA/FIS-OR02: Pamela Ferrari *Chemical poly ethyl methacrylate (PEMA) organogels for the removal of pressure sensitive tapes (PSTs) from paper artworks*
9.55 – 10.10	ABC/ANA/FIS-OR03: Nicole Bonelli *Surface cleaning of artworks: structure and dynamics of nanostructured fluids confined in a polymeric network*
10.10 – 10.25	ABC/ANA/FIS-OR04: Giovanna Poggi *Nanocomposites for the consolidation and deacidification of cellulose-based artifacts*
10.30 – 11.00	Coffee Break
*Sessione Congiunta**: Chimica Analitica -Fisica - Chimica dell'Ambiente e dei Beni Culturali***	
Chair: ***Luigia Sabbatini***	
11.00 – 11.25	ABC/ANA/FIS-KN02: Erika Ribechini, Laura Blanco-Zubiaguirre, Ilaria Degano, Jacopo La Nasa, Javier García-Iñañez, Maitane Olivares, Kepa Castro *GC/MS and HPLC/MS characterization of organic residues from ceramic vessels of Basque whalers of the* 16^{th} *to* 17^{th} *century*
11.25 – 11.40	ABC/ANA/FIS-OR05: Francesca Di Turo, Maria Teresa Doménech-Carbò, Noemì Montoya, Caterina De Vito, Fiorenzo Catalli, Gabriele Favero, Antonio Doménech-Carbò *FIB-FESEM-EDX study of silver Roman coins: characterization of the core microstructure and corrosion products with a multi-analytical approach*
11.40 – 11.55	ABC/ANA/FIS-OR06: Antonella Casoli, Clelia Isca, Stefano Volpin *I materiali e la tecnica pittorica di Konrad Witz nel suo capolavoro di Ginevra*
11.55 – 12.10	ABC/ANA/FIS-OR07: Elettra Barberis, Marcello Manfredi, Simone Baiocco, Eleonora Conte, Fabio Gosetti, Elisa Robotti, Pier Giorgio Righetti, Emilio Marengo *Towards the Non-invasive Protemic Analysis of Cultural Heritage and Archaeological Objects*
12.10 – 12.25	ABC/ANA/FIS-OR08: Giuseppe Egidio De Benedetto, Antonio Pennetta, Daniela Fico *Provenance of Bitumen from different Apulian Bronze Age settlements through a biomarker based approach*
12.25 – 12.40	ABC/ANA/FIS-OR09: Marzia Fantauzzi, Federica Cocco, Bernhard Elsener, Gabriele Navarra, Antonella Rossi *From XAES signals to depth-profile reconstruction: the case of copper and copper alloys*
12.40 – 13.00	ABC/ANA/FIS-OR10: Marco Orlandi, Luca Zoia, Anika Salanti, Diego Tamburini, Jeannette Jacqueline Łucejko, Francesca Modugno, Maria Perla Colombini *Integrated approach for the chemical characterization of archaeological woods*

13.00 – 14.00	Intervallo Pranzo

Sala Paestum B	
14.00 – 15.00	*Sessione Poster 1: Beni culturali, Ambiente, Equilibri* (ANA PO01-PO40)
Sala Paestum A	
Sessione Congiunta: ***Chimica Analitica - Elettrochimica - Gruppo Sensori***	
Chair: **Salvatore Daniele**	
15.00 – 15.30	ANA/ELE/GS-KN02: Andreas Lesch, Milica Jovic, Victor Costa Bassetto, Hubert H. Girault *Preparing Nanoparticles on Large Electrodes Using Inkjet Printing and Flash Light Irradiation*
15.30 – 15.50	ANA/ELE/GS-OR05: Stefania Rapino, Mirella Trinei, Alice Soldà, Marco Giorgio, Luca Bartolini, Matteo Iurlo, Massimo Marcaccio, Francesco Zerbetto, Pier Giuseppe Pelicci, Francesco Paolucci *Rapid, Low-cost and Portable Electrochemical Assay for Heart Injury Diagnosis*
15.50 – 16.10	ANA/ELE/GS-OR06: Maria Rita Tomei, Daniela Neagu, Fabiana Arduini, Danila Moscone *Carbon black modified screen-printed electrodes to detect chlorine dioxide.*
16.10 – 16.30	ANA/ELE/GS-OR07: Vincenzo Mazzaracchio, Daniela Neagu, Alessandro Porchetta, Giuseppe Palleschi, Daniela Moscone, Alice Pomponi, Giovanni Faggioni, Florigio Lista, Fabiana Arduini *Bacillus anthracis spore detection by using a label free impedimetric aptasensor*
16.30 – 17.00	Coffee Break
Sessione Parallela: ***Ambiente***	
Chair: **Claudio Minero**	
17.00 – 17.30	ANA-KN03: Silvia Becagli, Fabrizio Anello, Carlo Bommarito, Federico Cassola, Giulia Calzolai, Tatiana Di Iorio, Alcide di Sarra, Jose-Luis Gómez-Amo, Franco Lucarelli, Daniela Meloni, Silvia Nava, Giandomenico Pace, Mirko Severi, Damiano Massimiliano Sferlazzo, Rita Traversi, Roberto Udisti *Multidisciplinary approach to constrain the ship contribution to the aerosol of the Central Mediterranean Sea*
17.30 – 17.50	ANA-OR08: Noemi Colozza, Fabiana Arduini, Danila Moscone, Giuseppe Palleschi *A reagent-free paper-based biosensor for the detection of mustard agents*
17.50 – 18.10	ANA-OR09: Eleonora Conca, Mery Malandrino, Agnese Giacomino, Andrea Ruo Redda, Sandro Buoso, Marco Grotti, Ornella Abollino, Roberto Udisti *Development of a suitable sequential extraction procedure for the assessment of the availability and reactivity of metal species in Arctic PM10 samples*
18.10 – 18.30	ANA-OR10: Marianna Rossetti, Alessandro Porchetta, Francesco Ricci, Giuseppe Palleschi *DNA-based single step fluorescence detection of Domoic Acid in marine water*
18.30 – 20.00	***Assemblea della Divisione di Chimica Analitica***

Sala Olimpia

Sessione Parallela: **Scienza delle separazioni**	
Chair: **Alberto Cavazzini**	
15.00 – 15.30	ANA-KN04: Paola Donato, Veronica Inferrera, Daniele Giuffrida, Francesco Cacciola, Paola Dugo, Luigi Mondello *Supercritical fluid chromatography × reversed-phase liquid chromatography with quadrupole time-of-flight and ion mobility mass spectrometry detection: a proof of concept*
15.30 – 15.50	ANA-OR11: Carmela Maria Montone, Anna Laura Capriotti, Chiara Cavaliere, Riccardo Zenezini Chiozzi, Aldo Laganà *Development of an analytical strategy for the purification and identification of bioactive peptides from microalgae*
15.50 – 16.10	ANA-OR12: Martina Catani, Omar H. Ismail, Simona Felletti, Francesco Gasparrini, Alberto Cavazzini *Investigation of mass transfer phenomena in new core-shell and sub-2µm fully porous chiral stationary phases for ultrafast high-performance enantioseparations*
16.10 – 16.30	ANA-OR13: Valentina Marassi, Barbara Roda, Andrea Zattoni, Sonia Casolari, Pierluigi Reschiglian *Integration of separation-based analytical platforms in the development of nanomaterials as bioactive products*
16.30 – 17.00	Coffee Break
Sessione Parallela: **Equilibri in soluzione e speciazione**	
Chair: **Concetta De Stefano**	
17.00 – 17.20	ANA-OR14: Emilia Furia, Rosangela Elliani, Luana Malacaria, Antonio Tagarelli *Coumarin-3-carboxylic acid as ligand: acid-base properties, interactions with Fe3+and characterization of complexes in aqueous solution*
17.20 – 17.40	ANA-OR15: Denis Badocco, Valerio Di Marco, Alfonso Venzo, Marco Frasconi, Paolo Pastore *Ion pair formation between tertiary aliphatic amines and perchlorate in the biphasic H_2O / CH_2Cl_2 system*
17.40 – 18.00	ANA-OR16: Clemente Bretti, Rosalia Maria Cigala, Francesco Crea, Concetta De Stefano, Giuseppe Gattuso, Anna Irto, Gabriele Lando, Demetrio Milea, Silvio Sammartano *Acid-base and chelating properties of Gantrez copolymers*
18.00 – 18.20	ANA-OR17: Gaetano De Tommaso, Mauro Iuliano, Lucia De Rosa, Luca Domenico D'Andrea, Alessandra Romanelli, Gaetano Malgieri, Carla Isernia *Coordination of a bis-histidine oligopeptide with Ga^{3+} ion in aqueous solution*

	Sala Cassandra
Sessione Congiunta: **Chimica analitica - Spettrometria di massa**	
Chair: **Tommaso Cataldi**	
15.00 – 15.30	ANA/MAS-KN01: Cosima Damiana Calvano, Marco Glaciale, Sara Granafei, Anna Maria Sardanelli, Luana Bellanova, Antonella Mastrorocco, Francesco Palmisano, Tommaso Cataldi *Advanced mass spectrometric techniques for the untargeted lipidome characterization of fibroblasts in early on-set Parkinson's disease patients*
15.30 – 15.50	ANA/MAS-OR01: Simone Nicolardi, Yuri E.M. van der Burgt, Jeroen D.C. Codée, Manfred Wuhrer, Cornelis, H. Hokke, Fabrizio Chiodo *Structural characterization of bio-functionalized gold nanoparticles by ultrahigh resolution mass spectrometry*

15.50 – 16.10	ANA/MAS-OR02: Lucia Cenci, Graziano Guella, Alessandra Maria Bossi *Molecularly imprinted materials coupled to MALDI-TOF Mass Spectrometry for the targeted analysis of peptides and proteins*
16.10 – 16.30	ANA/MAS-OR03: Rossana Scarpone, Roberta Rosato, Federico Bacá, Manuel Sergi, Dario Compagnone *Unknown and non-target analysis to determine pesticides in fruit and vegetables by means of UHPLC-HRMS (Orbitrap)*
16.30 – 17.00	Coffee Break
Sessione Congiunta: ***Chimica analitica – Spettrometria di Massa***	
Chair: ***Paola Montoro***	
17.00 – 17.30	ANA/MAS-KN02: Danilo Sciarrone, Antonino Schepis, Luigi Mondello *Advanced analytical capabilities exploiting isotope ratio mass spectrometry and quadrupole mass spectrometry coupled to multidimensional gas chromatography*
17.30 – 17.50	ANA/MAS-OR04: Andreina Ricci, Paola Cimino, Anna Troiani, Federico Pepi, Stefania Garzoli, Chiara Salvitti and Vincenzo Barone *From ascorbic acid to furan molecules: a theoretical and experimental study on the gas phase acid catalyzed degradation of vitamin C*
17.50 – 18.10	ANA/MAS-OR05: Veronica Termopoli, Pierangela Palma, Giorgio Famiglini, Maurizio Piergiovanni, Achille Cappiello *Liquid-EI (LEI) Atmospheric Pressure Mechanism for the introduction of liquid streams into an unmodified electron ionization source of a mass spectrometer*
18.10 – 18.30	ANA/MAS-OR06: Chiara Salvitti, Andreina Ricci, Federico Pepi, Stefania Garzoli, Anna Troiani, Giulia De Petris, Marzio Rosi *Selective gas-phase conversion of D-fructose to 5-hydroxymethylfuraldehyde through a base-assisted dehydration process*

	Sale Paestum A
Sessione Parallela: ***Sensori***	
Chair: ***Danila Moscone***	
9.00 – 9.30	ANA-KN05: Giannetto Marco *Nanobiocomposite-based immunosensors for clinically significant biomarkers*
9.30 – 9.50	ANA-OR18: Maria Pesavento, Nunzio Cennamo, Luigi Zeni, Simone Marchetti *Development of a new platform for chemical sensors based on surface plasmon resonance and molecularly imprinted polymers as receptors*
9.50 – 10.10	ANA-OR19: Patrizia Romana Mussini, Serena Arnaboldi, Ivo Franco Buzzi, Mariacristina La Bianca, Gabriella Natale, Silvia Cauteruccio, Emanuela Licandro, Voichita Mihali, Francesco Sannicolò, Simona Rizzo, Armando Gennaro, Abdirisak Ahmed Isse *Enantioselective voltammetry on achiral electrodes: a comparison between inherently chiral additives based on different stereogenic element*
10.10 – 10.30	ANA-OR20: Paolo Bollella, Dmitry M. Hushpulian, Dónal Leech, Massimo Marcaccio, Gabriele Favero, Franco Mazzei, Lo Gorton, Riccarda Antiochia *Hydrogen peroxide sensitive and selective biosensors based on peroxidases from different sources wired by Os-polymer*
10.30 – 11.00	Coffee Break
Sessione Parallela: ***Metodologie Avanzate per la Bioanalitica***	
Chair: ***Elisa Robotti***	
11.00 – 11.30	ANA-KN06: Gosetti Fabio *Target and non-target LC-MS/MS strategies in environment, food and human health fields*
11.30 – 11.50	ANA-OR21: Ilario Losito, Laura Facchini, Tommaso Cataldi, Francesco Palmisano *Seasonal variations of major phospholipids in mussels of sp. Mytilus galloprovincialis: an investigation by hydrophilic interaction liquid chromatography-electrospray ionization Fourier-transform mass spectrometry*
11.50 – 12.10	ANA-OR22: Carlo Crescenzi, Giuliana Grasso, Francesco Iadaresta, Erik Holmgren *Applications of Porous Graphitic Carbon in liquid chromatography – mass spectrometry*
12.10 – 12.30	ANA-OR23: Pasquale Palladino, Maria Grazia Manera, Roberto Rella, Maria Minunni, Simona Scarano *Synthetic receptors for Troponin T detection by SPR transduction for acute myocardial infarction diagnosis*
12.30 - 12.50	ANA-OR24: Catia Contado *Nano- and micro-particles in food and consumer products: the role of the Field Flow Fractionation techniques in their characterization*
12.50 – 13.10	ANA-OR25: Daniela Cecconi, Marcello Manfredi, Jessica Brandi, Emilio Marengo *Evaluation and comparison of gel-based and gel-free approaches for the in-depth exploration of milk rice proteome*
13.00 – 14.00	Intervallo Pranzo

Sale Olimpia	
Sessione Parallela: ***Ambiente***	
Chair: ***Carlo Crescenzi***	
9.00 – 9.30	ANA-KN07: Marco Grotti, Andrea Bazzano, Francisco Ardini, Kris Latruwe, Frank Vanhaecke *New insight into the Pb and Sr isotopic compositions of environmental samples from polar regions via single- and multi-collector inductively coupled plasma mass spectrometry*
9.30 – 9.50	ANA-OR26: Francesco Iadaresta, Michele Manniello, Conny Östman, Carlo Crescenzi, Jan Holmbäck, Paola Russo *Aromatic Amines in Textile as Potential Threat for Human Health*
9.50 – 10.10	ANA-OR27: Attilio Naccarato, Antonella Tassone, Sacha Moretti, Rosangela Elliani, Francesca Sprovieri, Nicola Pirrone, Antonio Tagarelli *A greener approach for organophosphate flame retardant determination in airborne particulate matter: microwave-assisted extraction using hydroalcoholic mixture coupled with solid phase microextraction gas chromatography tandem mass spectrometry*
10.10 – 10.30	ANA-OR28: Ivan Notardonato, Mario Vincenzo Russo, Pasquale Avino *Ultrasound-Vortex-Assisted Liquid-Liquid Micro-Extraction for Simultaneous Determination of Organophosphorus Pesticides and Phthalates in Baby Foods*
10.30 – 11.00	Coffee Break

Sessione Parallela: ***Ambiente***	
Chair: ***Gianpiero Adami***	
11.00 – 11.20	ANA-OR29: Marina Di Carro, Barbara Benedetti, Cristiana Mirasole, Emanuele Magi *Calibration of commercial and modified Polar Organic Chemical Integrative Samplers (POCIS) for the analysis of emerging pollutants in waters*
11.40 – 12.00	ANA-OR31: Sandro Recchia, Carla Tiraboschi, Simone Tumiati, Carlo Dossi, Stefano Poli *Development of a prototype analytical apparatus for the quantitative determination of the composition of* fluids in synthetic rocks
12.00 – 12.20	ANA-OR32: Andrea Speltini, Francesca Merlo, Matteo Contini, Federica Maraschi, Michela Sturini, Lorenzo Malavasi, Antonella Profumo *Solid-phase extraction of trace glucocorticoids from environmental waters on silica-supported humic acids-derived carbons followed by HPLC-ESI-MS*
12.20 – 12.40	ANA-OR33: Alessandro Tinti, Lorenza, Corbella, Cristina Colombi, Eleonora Cuccia, Vorne Gianelle, Satoshi Takahama, Stefania Gilardoni, Paola Fermo *Aliphatic Amines In Atmospheric Aerosol: Sources And Distribution*
12.40 – 13.00	ANA-OR34: Rita Traversi, Silvia Becagli, Laura Caiazzo, Massimo Chiari, Giulia Calzolai, Fabio Giardi, Franco Lucarelli, Angelo Lupi, Mauro Mazzola, Boyan Petkov, Mirko Severi, Vito Vitale, Roberto Udisti *Elemental and Organic Carbon contribution to atmospheric aerosol at Ny Ålesund (Svalbard Islands)*

13.00 – 14.00	Intervallo Pranzo
	Sala Paestum B
14.00 – 15.00	*Sessione Poster 2: Scienza delle separzioni, Bioanalitica, Spettrometria di massa* (ANA PO41-PO85)

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Sala Paestum B	
14.00 – 15.00	*Sessione Poster 3: Elettrochimica-sensori, Spettroscopia, Chemiometria, Forense, poster "ultimo minuto"* (ANA PO86-PO140)
Sale Paestum A	
Conferenza Plenaria	
Chair: ***Giuseppe Palleschi***	
15.00 – 15.45	ANA-PL02: Francesco Ricci *DNA-based nanodevices for clinical application*

Sessione Parallela: ***Sensori-Elettrochimica***	
Chair: ***Giuseppe Palleschi***	
15.50 – 16.10	*Finalisti premio Levi* ANA-IN03: Alessia Amodio, Abimbola Feyisara Adedeji, Matteo Castronovo, Elisa Franco, Francesco Ricci *pH-controlled assembly of DNA tiles*
16.10 – 16.30	ANA-OR35: Alessandro Porchetta, Marianna Rossetti, Giuseppe Palleschi, Francesco Ricci *Co-localization of DNA-based conformational switches for Single-Step Fluorescence Detection of Antibodies*
16.30 – 17.00	Coffee Break
Sessione Parallela: Sensori-Elettrochimica	
Chair: ***Francesco Ricci***	
17.00 – 17.30	ANA-KN08: Simona Ranallo, Marianna Rossetti, Andrea Idili, Kevin W. Plaxco, Alexis Vallée-Bélisle, Giuseppe Palleschi, Francesco Ricci *Antibody powered DNA-based nanomachines*
17.30 – 17.50	ANA-OR36: Ilaria Palchetti, Francesca Bettazzi, Luigi Falciola, Valentina Pifferi, Anna Testolin, Chiara Ingrosso, Michela Corricelli *Colloidal Nanoparticle modified Graphene-based electrochemical platforms for clinical biomarker detection*
17.50 – 18.10	ANA-OR37: Donato Calabria, Cristiana Caliceti, Martina Zangheri, Mara Mirasoli, Patrizia Simoni, Aldo Roda *Smartphone–based enzymatic biosensor for rapid detection of oxidase substrates using confined multilayer paper reflectometry*
18.10 – 18.30	ANA-OR38: Stefano Cinti, Luca Fiore, Renato Massoud, Claudio Cortese, Danila Moscone, Giuseppe Palleschi, Fabiana Arduini *A reagentless paper-based screen-printed device to detect chloride ions in serum and sweat*
18.30 – 18.50	ANA-OR39: Donatella Coviello, Michela Contursi, Innocenzo Giuseppe Casella *PVA/GO/Au: development and characterization of a new electrode material*
8.50 – 19.10	ANA-OR40: Paolo Bollella, Daniela A. Stevar, Cristina Tortolini, Lo Gorton, Roland Ludwig, Harry Boer, Anu Koivula, Gabriele Favero, Riccarda Antiochia, Franco Mazzei *Glucose/Oxygen Enzymatic Fuel Cell based on a "green" Gold Nanoparticles modified Graphene Screen-printed Electrode for Glucose detection in human saliva*
19.10 – 19.30	ANA-OR41: Daniele Zappi, Serena Gabriele, Marta Letizia Antonelli, Claudia Sadun *Generation IV ionic liquids and nanomaterials to develop innovative electrochemical biosensing platforms*
Sala Olimpia	

Sessione Parallela: ***Scienza delle Separazioni***	
Chair: ***Alessandra Maria Bossi***	
15.50 – 16.10	ANA-OR42: Riccardo Zenezini Chiozzi, Francesca Ferraris, Carmela Maria Montone, Susy Piovesana, Aldo Laganà *Identification of bioactive peptides derived from cauliflower by-products by multidimensional liquid chromatography and bioinformatics*
16.10 – 16.30	ANA-OR43: Simone Marchetti, Maria Pesavento, Rachele Maria Adele Bernini, Domingo Pastran, Daniele Merli, Letizie DeMaria *Solid phase extraction of dibenzyl disulphide on a molecularly imprinted polymer*
16.30 – 17.00	Coffee Break
Sessione Parallela: ***Spettroscopia - Chemiometria***	
Chair: ***Giuseppe Spoto***	
17.00 – 17.30	ANA-KN09: Ángela I. López-Lorente, Angelo Tricase, Rosaria Anna Picca, Cinzia Di Franco, Maria Chiara Sportelli, Boris Mizaikoff, Christine Kranz, Antonio Valentini, Gerardo Palazzo, Nicola Cioffi *What's new and good in the aqueous synthesis of colloidal gold nanoparticles (AuNPs). A critical overview of AuNPs synthetic methods and their analytical applications*
17.30 – 17.50	ANA-OR44: Maria Chiara Sportelli, Annalisa Volpe, Margherita Izzi, Maurizio Clemente, Rosaria Anna Picca, Amalia Conte, Matteo Alessandro Del Nobile, Antonio Ancona, Nicola Cioffi *Analytical characterization of new composites for food packaging applications*
17.50 – 18.10	ANA-OR45: Marco Minella, Claudio Minero, Matteo Baudino *Photocatalytic transformation of C2Cl4 in gas phase under UV-irradiated TiO2*
18.10 – 18.30	ANA-OR46: Massimo Innocenti, Francesco Di Benedetto, Emanuele Salvietti, Andrea Giaccherini, Walter Giurlani, Francesco Carlà, Nicola Cioffi, Rosaria A. Picca, Enrico Berretti, Roberto Felice *Microscopic and Spectroscopic Analysis with Synchrotron Light of Modified Surfaces of Technological Interest*
18.30 – 18.50	ANA-OR47: Alessandra Biancolillo, Remo Bucci, Andrea Magrì, Federico Marini *Metodi multi-block per l'analisi degli alimenti*
18.50 – 19.10	ANA-OR48: Cristina Malegori, Paolo Oliveri, Maria Alessandra Boggiani, Graziella Pastorini, Monica Casale *An innovative NIR hyperspectral imaging approach to pattern cheese ripening*
19.10 – 19.30	ANA-OR49: Elisa Robotti, Marcello Manfredi, Elettra Barberis, Emilio Marengo *Development of a method for the quality control of polystyrene (EPS) based on the use of microscopy techniques and multivariate statistical methods*

	Sala Athena
Sessione Congiunta: ***Chimica analitica – Chimica dell'Ambiente e dei Beni Culturali***	
Chair: ***Fabrizio Passarini***	
15.00 – 15.25	ABC/ANA-KN01: Marco Pesce, Andrea Critto, Silvia Torresana, Monia Santini, Elisa Giubilato, Lisa Pizzol, Paola Mercogliano, Alberto Zirino, Ouyang Wei, Antonio Marcomini *An integrated modelling approach to study the impacts of nutrients on coastal aquatic ecosystems in the context of climate change*
15.25 – 15.50	ABC/ANA-KN02: Davide Vione, Birgit Koehler, Francesco Barsotti, Marco Minella, Claudio Minero, Lars J. Tranvik, Tomas Landelius *Photoinduced Processes in Surface Waters: A Photochemical Mapping of Sweden*
15.50 – 16.10	ABC/ANA-OR01: Luca Carena, Silvia Berto, Davide Vione, Federico Valmacco, Matteo Marletti, Agnese Giacomino, Claudia Barolo, Roberto Buscaino, Mery Malandrino *Application of an electro-activated glassy carbon electrode (GCE) to the analytical monitoring and photochemical studying of acetaminophen.*
16.10 – 16.30	ABC/ANA-OR02: Luca Rivoira, Alessandra Lo Re, Davide Vione, Marco Minella, Marta Appendini, Barbara Onida, Maria Concetta Bruzzoniti *Removal and photodegradation of glyphosate herbicide from waters using a mesoporous substrate with adsorbent properties*
16.30 – 17.00	Coffee Break
Sessione Congiunta: ***Chimica analitica – Chimica dell'Ambiente e dei Beni Culturali***	
Chair: ***Andrea Gambaro***	
17.00 – 17:30	ABC/ANA-KN03: Alessandra Genga, Maria Siciliano, Cosimino Malitesta, Tiziana Siciliano, Antonio Proto, Raffaele Cucciniello *Primary and secondary carbonaceous species in PM10 and PM2.5 samples*
17.30 – 17.50	ABC/ANA-OR03: Sara Padoan, Elena Barbaro, Matteo Feltracco, Roberta Zangrando, Carlo Barbante, Andrea Gambaro *Characterization of ionic composition in the submicron fraction of urban aerosol*
18.10 – 18.30	ABC/ANA-OR04: Mirko Severi, Silvia Becagli, Laura Caiazzo, Virginia Ciardini, Ester Colizza, Fabio Giardi, Karin Mezgec, Claudio Scarchilli, Barbara Stenni, Elizabeth R. Thomas, Rita Traversi, Roberto Udisti *Sea salt sodium record from Talos Dome (East Antarctica) as a potential proxy of the Antarctic past sea ice extent*
18.30 – 18.50	ABC/ANA-OR05: Roberto Udisti, Silvia Becagli, Ezio Bolzacchini, Laura Caiazzo, David Cappelletti, Luca Ferrero, Fabio Giardi, Marco Grotti, Angelo Lupi, Mery Malandrino, Mauro Mazzola, Beatrice Moroni, Mirko Severi, Rita Traversi, Vito Vitale *A six-year record of size distribution and chemical composition of Arctic aerosol. Main results and future bi-polar perspectives*
18.50 – 19.10	ABC/ANA-OR06: Janeth Tafur Marinos, Marco Ginepro, Vincenzo Zelano *Effects of biomass, temperature and thermochemical process on PAH concentration in biochar*
19.10 – 19.30	ABC/ANA-OR07: Ezio Bolzacchini, Luca Ferrero, Antonio Proto, Concetta Pironti, Raffaele Cucciniello, Oriana Motta, Cristiana Rizzi, Grisa Močnik, Lorenza Dall'Aglio, Chiara Rostagno *Particulate and gaseous indoor contamination at the Museum of "Last Supper" of Leonarndo Da Vinci: results from one year of monitoring activity*

Medaglie e Premi
della Divisione di Chimica Analitica

Medaglia "*Arnaldo Liberti*" - 2017

Prof. Aldo Laganà, *Università degli Studi di Roma "La Sapienza"*

Medaglia "*Canneri*" - 2017

Prof. ssa Luigia Sabbatini, *Università degli Studi di Bari "Aldo Moro"*

Premi alla Ricerca

***"Premio Giovane Ricercatore"* - 2017**

Dott. ssa Susy Piovesana, *Università degli Studi di Roma "La Sapienza"*

***"Premio di Laurea"* - 2017**

Dott. ssa Carmela Maria Montone, *Università degli Studi di Roma "La Sapienza"*

Conferenze Plenarie

- ANA PL01: Luisa Torsi, *Università degli Studi di Bari "Aldo Moro"*
- ANA PL02: Francesco Ricci, *Università degli Studi di Roma "Tor Vergata"*

Printable Organic Bioelectronics for Bioanalytical Detections at The Physical Limit: Is This Feasible?

Luisa Torsi[a]

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Counting the molecules present in a solution instead of assaying its concentration is the ultimate and visionary goal in chemical analysis. It's actuation however, necessarily requires reliable technologies that can "count" the molecules one by one. Such an approach would enable not only fundamental understanding of subtle effects in an affinity interaction likely hidden in ensemble measurements, but also it would pave the way to striking applications. Indeed, proteins and biomolecules detection at the physical limit are foreseen to generate ground-breaking technological fallouts such as for instance, label-free biosensors endowed with high selectivity as well as sub attomolar (10^{-18} M, aM) sensitivity for non-invasive label-free quantitative analysis of pathogens or diseases' markers in bio-fluids such as saliva or tears.

Interestingly, cells can track single molecules by decoding the response mediated by millions of highly packed receptors residing on their surface. By this mean, sperm cells sense few chemoattractants to localize the oocyte while rod cells on the retina respond to a single photon. Conversely, label-free single-molecule detection has been achieved so far by funnelling a large number of ligands into a sequence of single binding events through few recognition elements host on a nano-sized transducing interface. For instance, single DNA detection has been demonstrated using few bio-probes attached to a single nanotube transistor. An approach involving nano-devices is therefore inherently unable to track few cues in a milieu as either very high ligand concentrations or impractical long times are required. Conceptualizing cells' ability to track recognition events at the physical limit, the use of an electrolyte gated organic field-effect transistor bio-functionalized with highly packed antibodies is presented and the selective and reliable electronic detection of an extremely low concentration of affinity ligands is demonstrated.[1-5]

The present lecture thus aims at presenting an overview on the challenges and on the exciting perspectives for Analytical Chemistry and Chemistry in general, that are associated with the quantification of proteins down to few molecules. An outlook on the extremely high-performance level of millimetre-size organic bioelectronic sensors integrating a trillion of capturing molecules, will be provided showing that sub-aM detection limits can be reliably reached.[1] As cases of studies, the selective and ultra-sensitive assay of immunoglobulins and C-reactive protein in saliva will be discussed. The organic bioelectronic transistors used are mm-size, low-cost and are operated at physiologically relevant conditions as well as in human saliva setting the ground for a revolution in immunoassay for early bio-markers detection.

References
1. E. Macchia *et al.*; "A transistor bio-functionalized with a trillion of antibodies detects few affinity ligands"; *submitted.*
2. M.Y. Mulla *et al.*; "Capacitance-modulated transistor detects odorant binding protein chiral interactions"; *Nature Communication*, 2015, vol. *6*, pp. 6010.
3. E. Macchia *et al.*; "Organic bioelectronics probing conformational changes in surface confined proteins"; *Scientific Reports (Nature)*, 2016, vol. *6*, pp. 28085.
4**.** L. Torsi *et al.;* "Organic thin-film transistors as plastic analytical sensors"; *Analytical Chemistry*, 2005, vol. *77* (19), pp. 380–387.
5**.** M. Magliulo *et al.*; "Label-free C-reactive protein electronic detection with an electrolyte-gated organic field-effect transistor-based immunosensor"; *Analytical and Bioanalytical Chemistry*, 2016, vol. *408* (15), pp. 3943-3952.

DNA-Based Nanodevices For Clinical Applications

Francesco Ricci[a]

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DNA nanotechnology uses synthetic DNA (or nucleic acids) as a versatile material to rationally engineer nanoscale tools and molecular devices.

During this presentation, I will give an overview of the most representative and recent examples developed in our lab in this research field. More specifically, I will show how to exploit the designability of DNA to fabricate nature-inspired DNA-based nanodevices that are designed to undergo a conformational change (switch) upon binding to a specific input (pH[1-4], antibodies[5-6], enzymes[7], small molecules[8-10], etc.). This input-triggered conformational change can be used for diagnostic, drug-delivery or synthetic-biology applications.

References
1. Porchetta A. et al.; *J. Am. Chem. Soc.*, 2013, *135*, 13238.
2. Idili A. et al.; *J. Am. Chem. Soc.*, 2014, *136*, 5836.
3. Idili A. et al.; *Nano Lett.*, 2015, *15*, 5539.
4. Amodio A. et al.; *J. Am. Chem. Soc.*, 2016, *138*, 12735.
5. Ranallo S. et al.; *Angew. Chem.*, 2015, *54*, 13214.
6. Ranallo S. et al.; *Nat. Commun.*, 2017, *8*, 15150.
7. Del Grosso E. et al.; *Nano Lett.*, 2015, *15*, 8407.
8. Amodio A. et al.; *J. Am. Chem. Soc.*, 2014, *136*, 16469.
9. Porchetta A. et al.; *Nano Lett.*, 2015, *15*, 4467.
10. Mariottini D. et al.; *Nano Lett.*, 2017, *17*, 3225.

Keynote e Conferenze su invito

- ANA KN 01: Sara Bogialli, *Università degli Studi di Padova.*
- ANA KN 02: Martina Zangheri, *Università degli Studi di Bologna "Alma Mater Studiorum".*
- ANA/ELE/GS KN 01: Fabiana Arduini, *Università degli Studi di Roma "Tor Vergata".*
- ABC/ANA/FIS KN 01: Rocco Mazzeo, *Università degli Studi di Bologna "Alma Mater Studiorum".*
- ABC/ANA/FIS KN 02: Erika Ribechini, *Università degli Studi di Pisa.*
- ANA/ELE/GS KN02: Andreas Lesch, *École Polytechnique Fédérale de Lausanne (EPFL) Valais, Svizzera.*
- ANA KN 03: Silvia Becagli, *Università degli Studi di Firenze.*
- ANA KN 04: Paola Donato, *Università degli Studi di Messina.*
- ANA/MAS KN01: Cosima Damiana Calvano, *Università degli Studi di Bari "Aldo Moro".*
- ANA/MAS KN02: Danilo Sciarrone, *Università degli Studi di Messina.*
- ANA KN 05: Marco Giannetto, *Università degli Studi di Parma.*
- ANA KN 06: Fabio Gosetti, *Università degli Studi del Piemonte Orientale.*
- ANA KN 07: Marco Grotti, *Università degli Studi di Genova.*
- ANA KN 08: Simona Ranallo, *Università degli Studi di Roma "Tor Vergata".*
- ANA KN 09: Nicola Cioffi, *Università degli Studi di Bari "Aldo Moro".*
- ABC/ANA KN01: Antonio Marcomini, *Università degli Studi di Venezia "Ca' Foscari".*
- ABC/ANA KN02: Davide Vione, *Università degli Studi di Torino.*
- ABC/ANA KN03: Alessandra Genga, *Università del Salento.*
- ANA IN01: Susy Piovesana, *Università degli Studi di Roma "La Sapienza".*
- ANA IN02: Anna Laura Capriotti, *Università degli Studi di Roma "La Sapienza".*
- ANA IN03: Alessia Amodio, *Università degli Studi di Roma "Tor Vergata.*

High Resolution Mass Spectrometry: The Re-Evolution Of The Risk Assessment And Management

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The evolution and the spreading of high resolution mass spectrometry (HR-MS) coupled to gas or liquid chromatography (GC or LC) has suggested the implementation of new analytical workflows for the detection of unknown compounds. In the last ten years, a huge number of scientific papers based on HR-MS highlighted the presence of natural and synthetic organic substances that are of concerns in the environmental, food, clinical and forensic fields.

Anyway, the policy actions require much more information than those provided by the analytical screening, and the approach based on risk assessment is essential. It is clear that the chemical snapshot of a possible contamination is not exhaustive, and inter-sectorial expertise are necessary to correctly understand the health risks.

Actually, HRMS is still underused in the framework of the official analyses, even because the harmonization of the protocols and the data interpretation remain important drawbacks. Furthermore, the need of quantifying compounds with potential adverse toxicological effect is surely the challenge to be faced out.

Recently, some new trends has become more common among stakeholders involved in the risk management of the environment, such for the water analysis. The adoption of the Water Safety Plans is spurring the integration between the available analytical platforms based on HR-MS and the "decision making" actions.

Some of the main limitations and perspectives related to the revolution of the risk management inspired by the HR-MS is here presented and discussed.

Biosensors Based on Chemiluminescent-Lateral Flow Immunoassay: A Powerful Approach For Integrated Analytical Platforms

Martina Zangheri[a], Mara Mirasoli[a], Laura Anfossi[b], Fabio Di Nardo[b], Cristina Giovannoli[b], Massimo Guardigli[a], Claudio Baggiani[b], Aldo Roda[a]

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Lateral Flow Immunoassay (LFIA) is a technology currently widely applied in resource-poor or non-laboratory environments (point-of-care, POC) that is based on prefabricated strips of a carrier material containing dry reagents that are activated by applying the fluid sample. The conventional LFIA are available mostly for qualitative analyses, but the use of enzymes as tracers, coupled with chemiluminescence (CL) detection, provides highly sensitive quantitative assays[1]. Biosensors based on CL-LFIA are very promising analytical tools for rapid on-site detection of analytes in complex matrices.

Here, we report about the latest advances in CL-LFIA based technologies and their applications in different fields. Thanks to the intrinsic simplicity of CL detection principle, several portable and sensitive CL detectors can be designed to obtain a fully-integrated system. In addition, to reach the goal of portability, ready-to-use disposable cartridges containing all the reagents necessary to complete the analysis must be developed.

Nowadays, the improved imaging technology of the Back Side Illuminated Complementary Metal Oxide Semiconductor (BI-CMOS) sensors used in smartphone cameras make them suitable for fast and accurate POC diagnosis based on CL-LFIA[2-3]. These biosensors will be useful in all situations where a decentralized and fast detection is required, taking advantage of the location (GPS) and wireless long distance data transfer ability. We applied this technology in different fields, from the detection of clinical biomarkers to the evaluation of mycotoxins food contamination. In particular, different formats for the LFIA cartridges were designed for combining compactness and ease of use. Accessories able to transform the smartphone into a CL detector were developed using a desktop 3D printer.

Another CL detector suitable for on-site applications are thin film hydrogenated amorphous silicon (a-Si:H) photosensors[4] that have recently been proposed as a low-cost and versatile technology for developing a miniaturized biosensor with high detectability and sensitivity. We developed a novel biosensor based on CL-LFIA method with integrated amorphous silicon (a-Si:H) photosensors array to quantitatively detect human serum albumin (HSA) in urine samples. This combination provided compact, sensitive and potentially low-cost microdevices for CL and bioluminescence-based bioassays with a wide range of possible applications for in-field and POC bio-analyses.

Finally, the last challenge is to exploit the simplicity and portability of the CL-LFIA based device for performing salivary biomarker analysis onboard the International Space Station (ISS). A portable biosensor was developed for salivary cortisol quantitative detection, which will be used by crew members for monitoring their health status during space missions.

References
1. M. Zangheri, F. Di Nardo, L. Anfossi, C. Giovannoli, C. Baggiani, A. Roda, M. Mirasoli; *Analyst*, 2015, *140*, 358-365.
2. M. Zangheri, L. Cevenini, L. Anfossi, C. Baggiani, P. Simoni, F. Di Nardo, A. Roda; *Biosensors and Bioelectronics*, 2015, *64*, 63-68.
3. A. Roda, M. Guardigli, D. Calabria, M.M. Calabretta, L. Cevenini, E. Michelini; *Analyst*, 2014, *139*, 6494-650.
4. M. Zangheri, F. Di Nardo, L. Anfossi, M. Mirasoli, A. Nascetti, D. Caputo, G. De Cesare, M. Guardigli, C. Baggiani; *Analytical and Bioanalytical Chemistry*, 2016, *408*, 8869-8879.

New Sustainable and Cost-Effective Paper-Based Electrochemical (Bio)Sensors

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Electronic equipment generated 9 million tons of waste in 2005 in EU, and it is expected to grow to more than 12 million tons by 2020. To decrease the environmental pollution of electronics, the development of sustainable sensors, including paper-based electrochemical devices, are attracting growing interest thanks to their cost-effectiveness, suitability for in situ analysis, and environmentally friendly.

In this keynote, we reported the recent advancements on paper-based electrochemical (bio)sensors for environmental, biomedical, and agrifood sectors carried out by our group.

We described a novel reagentless paper-based electrochemical phosphate sensor, manufactured with a simple and inexpensive approach. By following three easy steps, consisting of wax patterning, paper chemical modification, and electrode screen-printing, the filter paper provides an effective electroanalytical platform to sense phosphate ions in standard solutions and in real samples (river water). This novel and highly sustainable configuration allows for the determination of phosphate ions with high reproducibility thanks to the use of heptamolybdate as reagent loaded on paper and carbon black as ink nanomodifier, achieving a detection limit of 4 mM. The filter paper has been also combined with the butyrylcholinesterase enzyme (BChE) for the detection of pesticides in rivers and wastewaters. The principle of this approach is based on dual electrochemical measurements, in parallel, of butyrylcholinesterase enzyme activity towards butyrylthiocholine, with and without exposure to contaminated samples. The sensitivity of this device is largely improved using a carbon black/Prussian Blue nanocomposite as a working electrode modifier. A strip of a nitrocellulose membrane, that contains the substrate, is integrated with a paper-based test area that holds a screen-printed electrode and BChE, allowing a reagent-free detection of Paraoxon down to 3 μg/L. Beside the filter paper, the office paper has also been exploited as substrate to print the electrode. An office-paper based sensor has been developed for monitoring Zn(II) in biological fluids. The printed sensor modified with bismuth film has been used to detect it by stripping analysis, with a detection limit of 25 ng/mL and a relative standard deviation of 8%. To highlight the feasibility, reliability, and easiness of the proposed electrochemical sensor, Zn(II) has been detected in serum and sweat at a physiological level (μg/mL). The sensor printed on office paper has been also combined with alcohol oxidase enzyme for the detection of ethanol in beer samples. After optimizing the analytical parameters, such as pH, enzyme, concentration, and working potential, the developed biosensor allowed a facile quantification of ethanol up to 10 mM, with a detection limit equal to 0.52 mM. Recently, we have also combined the sensor fabricated using wax printing and screen-printing technologies with a printed holder made by a 3-D printing technology. This device is able to measure the BChE activity in serum, with a linear range up to 12 UI/mL and a detection limit lower than 1 UI/mL.

Macro Mid-Infrared Total Reflection (MA-FTIR) Mapping for the Characterization of Outdoor Bronze Surfaces

Rocco Mazzeo[a], *Stjin Legrand*[b], *Giorgia Sciutto*[a], *Silvia Prati*[a], *Emilio Catelli*[a], *Paolo Oliveri*[c], *Koen Janssens*[b]

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In the last decades, many research efforts have been devoted to the development of advanced non-invasive approaches for the examination of cultural heritage. However, up to now, too few attentions has been paid on the potentialities of the Macro Mid-Infrared total reflection (MA-FTIR) mapping analysis. Indeed, the infrared reflectance spectroscopy single point investigation has been largely applied in analytical studies of artworks due to its advantage of characterizing both organic and inorganic materials. On the other hand, the possibility to simultaneously obtained information on molecular composition and spatial distribution of constituents is of crucial importance for properly addressing conservation issues.

To this aim, the present research work was focused on the application of an advanced MA-FTIR mapping system for the study of altered bronze surfaces. Moreover, an *ad hoc* multivariate approach has been proposed for the interpretation of data.

A bronze sculpture exposed in the atmosphere deteriorates with time, developing a greenish/blackish layer mainly constituted of corrosion products. The formation of these corrosion products implies complex chemical, electrochemical and physical processes that strongly depend on the constituents of the surrounding environment. In addition, different acrylic resins, synthetic waxes and organic inhibitors may be commonly applied for short-term protection of outdoor bronze sculptures.

To the Authors knowledge for the first time Mid FTIR macro mapping analysis was performed on metal patinas, allowing the location of corrosion products and old coatings, and describing their interactions. The performances of the approach have been initially evaluated on standard bronze samples characterized by the presence of a green basic hydroxysulfate (brochantite) treated with different organic materials. Subsequently, the exceptional case of study of the bronze sculptures of the Neptune Fountain (Bologna, 16th century) has been investigated.

The instrument acquired hyperspectral cubes by scanning the metal surface without any contact, recording sequential total reflection single-point spectra. The big dimension of the data cubes obtained, as well as, the deformation of IR bands induced by specular reflection phenomena, may serious hampering the correct interpretation of the spectral features. Thus, a chemometric method, based on the use of the brushing procedure, was proposed to extract all the useful information embedded in a complex hypercube.

The high specificity of MA-FTIR mapping revealed important outcomes on the state of conservation of the monumental statue. In particular, it was possible to clearly describe well preserved areas in which wax and incralac resulted to be still present, describing their distribution and identifying zones affected by a more aggressive corrosion process.

GC/MS and HPLC/MS Characterization of Organic Residues from Ceramic Vessels of Basque Whalers of the 16th to 17th Century

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The aim of this work is focused on the identification of the organic residues from ceramic vessels recovered from a deposit in Lekeitio (Basque Country, Northern Spain). These vessels are suspected to have been used by the Basque whalers in the period from 16th to 17th Century to store whale oil. Bearing in mind our aim, different analytical approaches based on chromatography and mass spectrometry (GC/MS and HPLC-ESI-qTOF) were used to study both fresh blubber and whale oil products and the archaeological substances in order to obtain chromatographic profiles and possibly detect highly diagnostic biomarkers. Two hydrolysis approaches were used in order to compare data and obtain as much information as possible; (i) microwave assisted direct hydrolysis of the ceramic samples and (ii) microwave assisted hydrolysis of previously solvent-extracted samples. On the other side, the study of solvent (chloroform:hexane (3:2 v/v)) soluble fraction was carried out by means of HPLC-ESI-qTOF. Preliminary results led to the identification of some interesting organic compounds in the hydrolysable and soluble aliquots from the ceramic vessel such as pristane, phytane, several saturated fatty acids, hydroxyacids and cholesterol along with triacylglycerols in the solvent soluble fraction. On the other hand, the obtained results for the fresh whale oil and blubber suggested a similar lipid profile to the ones obtained for the archaeological samples. The chemical results together with archaeological data seem to indicate the vessels were used to store whale oil.

Preparing Nanoparticles on Large Electrodes Using Inkjet Printing and Flash Light Irradiation

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Coating electrodes with catalytically active metal and alloyed metal nanoparticles (NPs) can improve significantly the performance of commercial electrocatalytic and (bio)analytical devices. Nevertheless, the price of many noble and scarce metals requires sustainable strategies to synthesize NPs and to prepare nanoparticle-decorated surfaces. In addition, the cost-effective and high-throughput optimization of the NP properties as a result of the NP size, shape, composition and synergistic effects with support materials is very attractive for academia as well as industry. This is especially true if process conditions are easily tunable, highly reproducible and fully up-scalable.

The fabrication of NP-coated electrode surfaces can be achieved in various ways, usually started with a NP synthesis, with or without support particles and dispersed in solution, before an ink or paste is formulated. Subsequently, this mixture is casted by dropping, dispensing or printing onto the sensing device structure. Afterwards, thermal post-processing results in the removal of solvents and stabilizers achieving electrodes with catalytically active and well-adhered NPs. Alternative strategies apply metal precursors that are electrochemically, (photo)chemically or thermally (thermal decomposition by equilibrium heating in a furnace) converted into the according NPs.

In this contribution, we demonstrate our novel approach where defined thin films of metal precursors, e.g. chloroplatinic acid, are first deposited onto various electrode surfaces by using inkjet printing and then irradiated with a high energy light pulse from a Xenon flash lamp to generate NPs within a fraction of a second[1]. Due to the rapid absorption of the flash light by the precursor-coated electrodes temperatures of several hundred degrees Celsius are generated immediately inside the printed films. The result is a rapid thermal decomposition of the precursor into the pure metal or alloyed metal nanoparticles. As for the well-known thermal decomposition processes at equilibrium heating conditions, side products are simply gaseous (e.g. HCl, Cl_2 and H_2O) leaving pure metal on the electrode surface[2,3].

We use an integrated inkjet printing (with three printheads) and flash light irradiation platform to prepare the NP-decorated electrodes (e.g. Pt deposited on ITO, graphene or carbon nanotubes) of square centimeter size only within few minutes at ambient conditions[4]. This allows a rapid optimization and up-scaling of the process outcome. The final electrodes were optically and electrochemically analyzed, the latter in particular with Soft-Probe Scanning ElectroChemical Microscopy (Soft-Probe-SECM)[5].

References
1. A. Lesch; *submitted.*
2. K. Jang, S. Yu, S. H. Park, H. S. Kim, H. Ahn; *J. Alloys Compd.*, 2014, *618*, 227-232.
3. S. H. Park, H. S. Kim; *J. Electrochem. Soc.*, 2015, *162*, F204-F210.
4. A. Lesch, F. Cortés-Salazar, V. Costa Bassetto, V. Amstutz, H. H. Girault; *Chimia*, 2015, *69*, 284-289.
5. A. Lesch, B. Vaske, F. Meiners, D. Momotenko, F. Cortés-Salazar, H. H. Girault, G. Wittstock; *Angew. Chem. Int.*, 2012, *51*, 10413-10416.

Multidisciplinary Approach to Constrain the Ship Contribution to the Aerosol of the Central Mediterranean Sea

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Ship emissions may significantly affect atmospheric concentrations of several important pollutants, especially in maritime and coastal areas[1]. In spite of the great amount of gas and particulate arising from ship emission, maritime transport is relatively clean if calculated per kilogram of transported material, and it is currently increasing with respect to air and road transport[2]. In addition, emissions from other transport sectors are decreasing due to the implementation of advanced emission reduction technologies, and the relative impact of shipping emissions is increasing. PM_{10} aerosol samples were collected during summer 2013 within the framework of the Chemistry and Aerosol Mediterranean Experiment (ChArMEx) at two sites located North (Capo Granitola, 36.6°N, 12.6°E) and South (Lampedusa Island, 35.5°N, 12.6°E), respectively, of the main Mediterranean shipping route in the Sicily Channel. The PM_{10} samples were collected with 12 hours time resolution at both sites. Selected metals, main anions, cations, and elemental and organic carbon were determined. The evolution of soluble V and Ni concentrations (typical markers of heavy fuel oil combustion) was related to meteorology and ship traffic intensity in the Sicily Channel, using a high resolution regional model for back trajectories calculation. Elevated concentration of V and Ni were associated with transport from the Sicily Channel and coincidences between trajectories and positions of large ships, both at Capo Granitola and Lampedusa; the vertical structure of the planetary boundary layer also appears to play a role, with high V values associated with strong inversions and stable boundary layer. The V concentration was generally lower at Lampedusa than at Capo Granitola, where it reached a peak value of 40 ng/m^3. Concentrations of rare earth elements, La and Ce in particular, were used to identify possible contributions from refineries, whose emissions are also characterized by elevated V and Ni amounts; refinery emissions are expected to display high La/Ce and La/V ratios, due to the use of La in the fluid catalytic converter systems. In general, low La/Ce and La/V ratios were observed in the PM samples, allowing to unambiguously identify the large role of the ship source in the Sicily Channel. Based on the sampled aerosols, ratios of the main aerosol species arising from ship emission with respect to V were estimated with the aim of deriving a lower limit for the total ship contribution to PM_{10}. The estimated minimum ship emission contributions to PM_{10} was 1.9 μg/m^3 at Lampedusa, and 2.8 μg/m^3 at Capo Granitola, corresponding to 11% and 8.2% of PM_{10}, respectively.

References
1. Endresen Ø., Sørgård E., Sundet J. K., Dalsøren S. B., Isaksen I. S. A., Berglen T. F. and Gravir G.; "Emissions from International Sea Transportation and Environmental Impact"; *J. Geophys. Res.*, 2003, *108*, 4560, doi:10.1029/2002JD002898.
2. Grewal D., Haugstetter H., "Capturing and Sharing Knowledge in Supply Chains in the Maritime Transport Sector: Critical Issues"; *Maritime Policy & Management*, 2007, 169-183.

Supercritical Fluid Chromatography × Reversed-Phase Liquid Chromatography with Quadrupole Time-Of-Flight and Ion Mobility Mass Spectrometry Detection: a Proof of Concept

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On line comprehensive liquid chromatography LC×LC techniques are becoming increasingly popular when dealing with separation of complex mixtures of non-volatile components. The maximum gain in separation power arises from the combination of independent separation mechanisms (stationary phases) and, to this regard, the combination of normal phase (NP) and reversed phase (RP) represents one of the most effective ways to increase orthogonality. However such a coupling poses important technical challenges, mainly related to the immiscibility of the mobile phases, peak focusing at the head of the secondary column (^{2}D), and signal interferences. On the other hand, seemingly compatible systems, such as RP-LC×RP-LC, suffer from high correlation of the separation, and peak deterioration due to viscous fingering effects.

Supercritical fluid chromatography (SFC) may be a valuable alternative to NP-LC in the first separation (^{1}D) dimension, delivering complementary selectivity while alleviating immiscibility issues and further providing a number of advantages related to the use of supercritical CO_2.

Here the development of a fully automated SFC × RP-LC instrument is described, configured around two 2-position, six-port high pressure switching valves equipped with two packed octadecyl silica cartridges for effective trapping and focusing of the analytes after elution from ^{1}D. After depressurization of the effluent by the backpressure regulator (BPR), a water make-up flow was added prior to entering the loops, to efficiently focus the solutes on the sorbent material and reduce interferences of expanded CO_2 gas on the second dimension separation.

In addition to PDA and QToF-MS detection, ion mobility separation based on analyte mass, shape and size added a fourth separation dimension for a comprehensive characterization of the sample. With such a system, carotenoids fingerprinting by in a paprika sample was obtained in half the time with respect to conventional NP-LC×RP-LC, with superior resolution in ^{2}D and extended ^{2}D column lifetime. The separation of geometric isomers like cis/trans carotenoids differing in collision cross-sections was demonstrated, using travelling wave ion mobility.

Advanced Mass Spectrometric Techniques for the Untargeted Lipidome Characterization of Fibroblasts in Early On-Set Parkinson's Disease Patients

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Parkinson's disease (PD) is a progressive neurodegenerative disease involving the nigrostriatal pathway, where patients manifest dysfunction in motor symptoms when more than 50% of neurons are lost [1]. Although it is well recognized that alterations of lipid signaling and metabolism plays a significant role in many human diseases [2], little is known about the role of lipids associated with this specific disease. Recently, it has been reported that altered lipid pathways in the primary visual cortex and the anterior cingulate are possible in neurological disorders such as PD by analyzing post-mortem tissues from patients in advanced neuronal degeneration stage [3]. Such an approach, however, hinders the identification of the first neuronal changes. Thus, understanding the mechanisms of PD and identifying neuronal changes in the early phase of PD, by recurring to samples alternative to post-mortem biopsies, represents an urgent and challenging task.

According to their polygenic predisposition and environmental etiopathology [4], skin fibroblasts are now widely recognized as a useful model of primary human cells, capable of reflecting the chronological and biological aging of the patients. A lipidomics study of easily accessible primary human fibroblasts is presented here based on hydrophilic interaction liquid chromatography coupled to electrospray ionization-Fourier transform mass spectrometry, using both positive and negative polarities [5]. After testing different extraction protocols, the Bligh-Dyer method was shown to provide the largest number of recovered lipids. Thus, phospholipids (PL) from dermal fibroblasts of two unrelated PD patients with different parkin mutations and two controls were characterized by recurring to single and tandem MS measurements on a hybrid quadrupole-Orbitrap mass spectrometer. This untargeted approach enabled the identification of various PL classes as phosphatidylcholines (PC), phosphatidylethanolamines (PE), lysoPC, lysoPE, phosphatidylinositols, phosphatidylserines, sphingomyelins, mono-, di- and tri-hexosylceramides and ganglioside GM1, GM2 and GM3. To identify the main lipids and/or lipid classes involved in the pathological condition of PD, lipidomics data on a higher number of samples need to be collected and processed by multivariate statistical analyses. In this communication, an interesting set of preliminary findings will be reported and discussed.

Acknowledgments

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References:
1. M.M. Wiest et al. *Curr. Opin. Lipidol*. 18 (2007) 1816.
2. T. Klockgether, *Cell Tissue Res*. 318 (2004) 115–120.
3. K. Farmer et al., *Int. J. Mol. Sci*. 16 (2015) 18865-18877.
4. J. Romaní-Aumedes et al., *Cell Death Disease* 5 (2014) 1364.
5. S. Granafei et al., *Anal Bioanal Chem* 407 (2015) 6391-6404.

Advanced Analytical Capabilities Exploiting Isotope Ratio Mass Spectrometry and Quadrupole Mass Spectrometry Coupled to Multidimensional Gas Chromatography

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

Nanobiocomposite-Based Immunosensors for Clinically Significant Biomarkers

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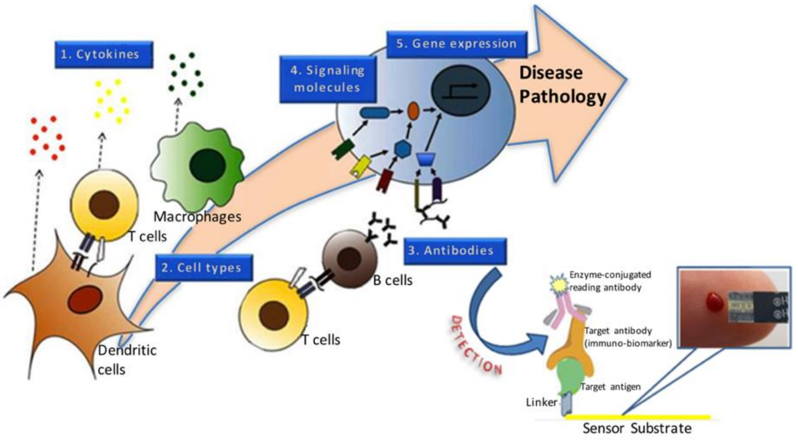
An outlook on the diagnostic applications of nanobiocomposite-based immunosensors implemented on the working principle of competitive or noncompetitive ELISA assays is given with an emphasis on applications in life sciences. Among biosensors, electrochemical immunosensors are very powerful and versatile tools for rapid and user-friendly screening analysis of biomarkers of clinical concern[1], thanks to their compatibility with portable and compact instrumentation, exploiting disposable screen-printed electrodes as sensing substrates[2]. These devices match the fundamental needs required for the screening analysis of biological samples in terms of reliability, simplicity of operation and of the analytical platform, fast response time and cost-effectiveness, associated to good sensitivity and specificity assured by targeted antibodies.



Enhanced analytical performance required for diagnostic purposes can be achieved exploiting the peculiar features of atomic or molecular nanomaterials, such as gold nanoparticles, carbon nanotubes and dendrimers, properly conjugated with the target bioreceptors. Nanobiocomposite-based immunosensors exhibit improved sensitivity thanks to their high active surface area, associated to the enhancement of the electron transfer in the diffusive phenomena involved in the transduction mechanisms. In addition, due to the absence of significant matrix effect, these devices are particularly suitable for direct analysis of physiological fluids, with excellent LODs achievable under careful optimization of the operating conditions. In this context, all the developed devices here described were optimized by multivariate experimental design approach and fully validated in different physiological fluids for determination of protein biomarkers (antigens, antibodies or enzymes) specifically related to oncological, autoimmune or infective diseases[3-8].

References
1. F. Bianchi, M. Giannetto, M. Careri; *Anal. Bioanal. Chem.*, 2014, 15-20.
2. R.A.S. Couto, J.L.F.C. Lima, M.B. Quinaz; *Recent developments*, *Talanta*, 2016, 801-814.
3. M. Giannetto, L. Elviri, M. Careri, M. A. Mangia, G. Mori; *Biosens. Bioelectron.*, 2011, 2232-2236.
4. M. Giannetto, L. Mori, G. Mori, M. Careri, A. Mangia; *Sens. Act. B*, 2011, 185-192.
5. M. Giannetto, M. Mattarozzi, E. Umiltà, A. Manfredi, S. Quaglia, M. Careri; *Biosens. Bioelectron*., 2014, 325-330.
6. A. Manfredi, M. Mattarozzi, M. Giannetto, M. Careri; *Sens. Act. B*, 2014, 300-307.
7. M. Giannetto, M.V. Bianchi, M. Mattarozzi, M. Careri; *Anal. Chim. Acta*, submitted.
8. M. Giannetto, M. Costantini, M. Mattarozzi, M. Careri; *RSC Adv.*, submitted.

Target and Non-Target LC-MS/MS Strategies in Environment, Food and Human Health Fields

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In the last years, modern LC-MS/MS technique have experienced an impressive progress, both in terms of technology development and application.

Identification of unknown analytes in complex samples has always represented one of the challenge for analytical chemistry. LC-MS/MS techniques can give an answer, supporting the so-called non-target analysis, a recent analytical strategy, which aims to give the comprehensive identification and quantification of the chemical species of interest in complex samples.

The versatility of LC-MS/MS technique not only permits the development of sensitive, precise and accurate methods for the identification and quantification of target species, but also the possibility of searching for non-target compounds without having any *a priori* knowledge about them.

The increasing use of hybrid MS analyzers and in particular high-resolution MS ones allowed the growth of non-target strategies, not only by using the traditional data dependent mode, but also through the data independent acquisitions.

Water-pollutant monitoring makes typically use of methods developed for target analysis, focused on priority pollutants. However, the monitoring of target-compounds is often insufficient to definitely assess the quality of surface water, because the presence of only a limited number of potential pollutants is considered, whereas the simultaneous presence of potentially harmful non-target pollutants must be taken into account. For example, pollutants can undergo degradation for action of sunlight, temperature, and bacteria, forming transformation products often more toxic than their precursors. The degradation studies of some pesticides in paddy water permitted to develop simultaneously target and non-target methods through the data independent acquisition mode.

In the field of food analysis, it is possible to investigate the modifications taking place in food and beverages to identify toxic or hazardous species that may form, because of reactions occurring among different ingredients, transformation reactions, environmental effects or releases from packaging materials. These potential interactions take generally place in post-production phases and during the pre-selling storage and conservation. The interactions are often unpredictable and can give rise to different types of contamination with the formation of new species potentially harmful to the health, For example, the photoirradiation of the beverages containing food dyes can cause the formation of degradation products due to interactions with the other components of the beverage itself. The elucidation of the degradation product chemical structures has been proposed on the basis of HR MS/MS acquired data.

Recent studies in human health field concern the topic of premature newborns to investigate the possible correlation with the presence and accumulation in newborn plasma of endocrine disrupting compounds (EDCs). Premature infants need intensive medical care and they must be nourished only with parenteral solutions by different medical devices for almost 2-3 months. For this purpose, a high throughput online SPE UHPLC-MS/MS method has been developed and allowed the determination of 21 EDCs in plasma samples of premature newborns and in the physiological solutions used for leaching experiments from these medical devices.

New Insight into the Pb and Sr Isotopic Compositions of Environmental Samples from Polar Regions via Single- and Multi-Collector Inductively Coupled Plasma Mass Spectrometry

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Measurement of isotope ratios is considered a hot topic for both the analytical and geochemical scientific communities because of the unique information that they can reveal. In particular, in the context of environmental studies, Pb and Sr isotope ratios can help to discriminate between natural and anthropogenic inputs, as well as to identify their source regions and transport pathways.

Pb shows pronounced variation in its isotopic composition because three out of its four isotopes, ^{206}Pb, ^{207}Pb and ^{208}Pb, are the stable end products of the decay chains of ^{238}U, ^{235}U and ^{232}Th, respectively. As a consequence, there are relatively large differences in the ^{208}Pb/^{207}Pb and ^{206}Pb/^{207}Pb values for crustal and ore Pb deriving from various locations and mining areas. Contrary to Pb, Sr is typically of natural origin; however, since ^{87}Sr is produced via the β^--decay of ^{87}Rb, natural variations of ^{87}Sr/^{86}Sr in rocks occur, and the determination of this isotope ratio can be used for tracing the geographical source(s) of mineral dust.

The accurate measurement of Pb and Sr isotope ratios in environmental samples collected from polar regions can, however, be quite challenging, due to the low analytical concentration, matrix effects, risk of contamination and the limited sample size.

In recent years, we have developed new analytical procedures based on both single- and multi-collector inductively coupled plasma mass spectrometry, able to provide fit-for-purpose performances for a number of environmental matrices, including marine suspended particulate matter and sediment, atmospheric particulate and surface snow. The methods were fully validated and successfully applied in the context of polar studies performed in both the Arctic (Ny-Ålesund, Svalbard Islands) and Antarctica (Terra Nova Bay and Dome Concordia).

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

Antibody powered DNA-based nanomachines

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Taking inspiration from naturally-occurring receptors, which often signal the presence of their molecular target via binding-induced conformational changes, we developed two different DNA-based nanomachines that are activated by specific antibodies. More specifically, in the first case we designed a conformational switching, optically signaling stem-loop DNA nanodevice that supports the introduction of two copies of a wide range of polypeptide, small molecule, or oligonucleotide recognition elements (1). The binding of the antibody to the DNA nanomachine causes a structural change, producing a fluorescence signal monotonically related to the target's concentration. The nanomachine can be adapted to the detection of any antibody by simply changing the recognition element. Moreover the nanomachine does not need to be chemically activated, it is rapid (acting within five minutes) enabling the targeted antibodies to be easily detected, even in complex clinical samples such as blood serum and may prove to be useful in a range of different applications such as point-of-care diagnostics and bioimaging.

In the second case, we have designed a new class of DNA based nanomachines that can reversibly load and release a molecular cargo upon the binding of a target antibody. Our strategy to rationally design an antibody-driven DNA-based nanomachine involves the use of a triplex forming DNA strand that is designed to recognize a specific DNA strand through the formation of a clamp-like triplex forming mechanism that involves both Watson-Crick and Hoogsteen interactions and which is conjugated at the two ends with a pair of antigens (2). Antibody binding to the two antigen tags in the nanomachine causes a conformational change that energetically disrupts the triplex-forming Hoogsteen interactions in the triplex complex thus destabilizing the nanomachine/cargo complex. The design principle for antibody-powered release of a molecular cargo strand is highly generalizable and can easily be adapted to other antibodies via the expedient of changing the recognition element employed. We have demonstrated here that our approach can be extended to different triggering antibodies and the effect can be specific and selective enough even in complex media (90% serum).

Given these attributes, the antibody-poweered DNA nanomachines we have developed here may prove of utility in a range of applications, including point-of-care diagnostics, controlled drug-release and in-vivo imaging.

(1) Ranallo S, Rossetti M, Plaxco KW, Vallée-Bélisle A, Ricci F. A Modular, DNA-Based Beacon for Single-Step Fluorescence Detection of Antibodies and Other Proteins, Angew. Chem. Int. Ed. 2015, 54, 13214–13218.
(2) Ranallo S, Prévost-Tremblay C, Vallée-Bélisle A, Ricci F. Antibody powered nucleic acid release using a DNA-based nanomachine. Nat. Comm. 2017, 2017, 8, 15150.

What's New and Good in the Aqueous Synthesis of Colloidal Gold Nanoparticles (AuNPs). A critical Overview of AuNPs Synthetic Methods and their Analytical Applications.

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Gold nanoparticles (AuNPs) are receiving increasing attention in several fields, such as biomedicine[1], sensors[2] and nanoparticle-assisted spectroscopies[3] and spectrometry[4], just to cite a few. Among the methods for AuNPs preparation, the chemical reduction of gold(III) species is widely applied, based on the use of tetrachloroauric acid ($HAuCl_4$) as precursor and sodium citrate or thiols as reducing/stabilizing agents[5-6]. In these cases, byproducts and adsorbates that may affect negatively the quality of the colloid are often present. Biosynthesized colloidal gold nanoparticles are remarkably attractive in several biomedical applications, due to their unusual physico-chemical properties, facile surface modification, and high biocompatibility[7]. However, chemical purity of these colloids is usually affected by the massive presence of biological matrices, which generally compose the synthesis medium (culture broth in case of microorganism-assisted biosynthesis, vegetal extracts, etc.). Moving to physical methods, laser ablation in liquid is a very promising technique for the synthesis of naked aqueous AuNP colloids although the reason of their stability in absence of stabilizers is yet matter of debate. Ultrapure AuNPs can be easily produced in water and many other solvents, having a fine control on morphological and physicochemical properties by changing laser experimental parameters[8,9]. Coming back to wet-chemical approaches, recently, few research groups have proposed the use of a solid reductant to assist the synthesis of AuNPs[9-12]. In this novel approach, stainless steel can be used as removable reducing substrate, in the aqueous preparation of gold nanocolloids. This innovative bottom-up method is very easy, quick and cost-effective, allowing the synthesis of highly stable NPs without any additional organic capping agent. However, the mechanisms behind this reaction are not yet fully understood. Very recently, we evaluated the effects on this system of several parameters (e.g. reaction time, precursor concentration, ionic strength, steel composition, etc.). In this keynote communication, we will provide an overview of the aforementioned approaches and we will critically evaluate their performance level in terms of AuNPs composition and properties (as per detailed spectroscopic and morphological analyses). Analytical applications of AuNPs will be thoroughly discussed, as well.

References
1. R.A. Rippel, A.M. Seifalian; *Journal of Nanoscience and Nanotechnology*, 2011, *11*, 3740.
2. K. Saha, S.S. Agasti, C. Kim, X. Li, V.M. Rotello; *Chemical Reviews*, 2012, *112*, 2739.
3. J. Huang, L. Zhang, B. Chen, N. Ji, F. Chen, Y. Zhanga, Z. Zhang; *Nanoscale*, 2010, *2*, 2733.
4. R.A. Picca, C.D. Calvano, N. Cioffi, F. Palmisano; *Nanomaterials*, 2017, *7*, 75 and references therein.
5. P. Zhao, N. Li, D. Astruc; *Coordination Chemistry Reviews*, 2013, *257*, 638.
6. M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman; *J. Chem. Soc. Chem. Commun.*, 1994, 801.
7. T.J. Park, K.G. Lee, S.Y. Lee; *Applied Microbiology and Biotechnology*, 2016, *100*, 521.
8. M. Rafique, M.S. Rafique, S.H. Butt, U. Kalsoom, A. Afzal, S. Anjum, A. Usman; *Optik*, 2017, *134*, 140.
9. V. Amendola, M. Meneghetti; *Phys. Chem. Chem. Phys.*, 2009, *11*, 3805.
10. T.H. Han, M.M. Khan, S. Kalathil, J. Lee, M.H. Cho; *Journal of Nanoscience & Nanotechnology*, 2013, *13*, 6140.
11. A.I. López-Lorente, B.M. Simonet, M. Valcárcel, S. Eppler, R. Schindl, C. Kranz, B. Mizaikoff; *Talanta*, 2014, *118*, 321.
12. A.I. López-Lorente, M. Valcárcel, B. Mizaikoff; *Microchim. Acta*, 2014, *181*, 1101.

An Integrated Modelling Approach to Study the Impacts of Nutrients on Coastal Aquatic Ecosystems in the Context of Climate Change

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Increase of atmospheric greenhouse gases (GHGs) due to anthropogenic activities is causing changes in Earth's climate. Global mean temperatures are expected to rise by 0.3 to 4.8 °C by the end of the 21st century, and the water cycle to be affected by changes in global atmospheric moisture. Coastal waterbodies such as estuaries, bays and lagoons, together with the ecological and socio-economic services they provide, could be most affected by the ongoing changes on climate being subjected to the combined changes in the physico-chemical processes of atmosphere, upstream land and coastal waters. Particularly, climate change is expected to alter phytoplankton communities by changing climate and environmental drivers such as temperature, precipitation, nutrient loadings and concentrations, and to exacerbate the symptoms of eutrophication events such as hypoxia, harmful algal blooms and loss of habitat. A better understanding of the links between environmental drivers and phytoplankton communities is necessary for predicting climate change impacts on aquatic ecosystems. In this context, the integration of climate scenarios and environmental models is a valuable tool for the investigation and prediction of phytoplankton ecosystem dynamics under climate change conditions. In the last decade, the impact of climate change on the environmental distribution and cycling of nutrients, including effects on aquatic ecosystems, prompted modeling studies at a catchment scale, mainly related to lake ecosystems. The further development of integrated modeling approaches to other types of waterbodies such as coastal waters can be a useful contribution to increase the availability of management tools for ecological conservation and adaptation policies. Here we present the case study of the Zero river basin (ZRB) in Italy, one of the main contributors of freshwater and nutrients loadings to the salt-marsh Palude di Cona (PDC), a waterbody belonging to the lagoon of Venice. To predict the impacts of climate change on nitrogen (N) and phosphorus (P) loadings of the ZRB and the consequent effects on the coastal phytoplankton community of PDC, we applied an approach integrating an ensemble of GCM-RCM climate projections, the hydrological model SWAT and the ecological model AQUATOX. Climate scenarios for the area indicated an increase of precipitations in the winter period and a decrease in the summer months, while temperatures show a significant increase over the year. The hydrological model SWAT predicted changes in water discharge and nutrient loadings of the ZRB, pointing out an increase in the winter period and a reduction during the summer months for both parameters. Simulations with AQUATOX predicted changes in water temperature, nutrient concentrations and N:P ratios, and consequent variations in the biomass and composition of phytoplankton in PDC, with major changes observed in the spring-summer period, where the abundance of warm-adapted species increases noticeably[1].

Reference

1. Pesce et *al.*; 2017.

Photoinduced Processes in Surface Waters: A Photochemical Mapping of Sweden

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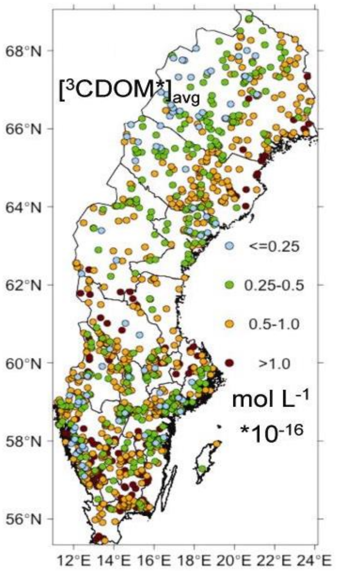
Photochemical reactions induce the self-depuration of surface waters, particularly against polar biorefractory pollutants that include many emerging contaminants[1]. Photoreactions are divided into direct photolysis and indirect photochemistry. Direct photolysis involves sunlight-absorbing pollutants, and transformation is triggered by photon absorption. Indirect photochemistry takes place when sunlight is absorbed by naturally occurring compounds called photosensitisers (e.g., nitrate, nitrite and chromophoric dissolved organic matter, CDOM) to produce reactive transient species such as the hydroxyl ($^{\bullet}$OH) and carbonate ($CO_3^{\bullet-}$) radicals, singlet oxygen ($^1O_2$), and CDOM triplet states (^{3}CDOM*)[2,3]. We have recently modeled photochemical processes in surface waters[4], predicting the phototransformation kinetics of pollutants and deriving photochemical parameters from available time series of water chemistry. In the latter case, one can get insight into the impact of climate change over photochemistry[5]. Here we show the application of photochemical modeling to data from a large geographic region. Based on a wide dataset that includes over 1000 Swedish lakes with their average depth, water chemistry and the incident sunlight irradiance, we could predict the steady-state [$^{\bullet}$OH], [$CO_3^{\bullet-}$], [$^1O_2$] and [^{3}CDOM*]. This is the first ever photochemical mapping of a country's inland waters. The model results were validated by comparison of available field data with the predicted photochemical lifetimes of carbamazepine and ibuprofen in Lake Boren[6]. Based on the photochemical map, and compared to temperate lakes, the CDOM-rich boreal lakes of Sweden are dominated by ^{3}CDOM* processes (except for the lakes located in the NW part of the country). In contrast, the efficient scavenging of $^{\bullet}$OH and $CO_3^{\bullet-}$ limits the importance of the relevant reactions. The ^{3}CDOM* processes are particularly effective towards the degradation of phenols, phenylurea herbicides and sulfonamide antibiotics[7]. CDOM is a key photosensitiser in most Swedish lakes and strongly prevails over nitrate and nitrite. Climate change is expected to produce water browning in boreal lakes including the Swedish ones, due to export of light-absorbing organic compounds from soil to surface waters[8]. Browning enhances the levels of CDOM, which is the ^{3}CDOM* precursor. Therefore, the importance of the ^{3}CDOM*-induced processes is expected to increase even more in the future, in Swedish lakes as well as in many other boreal areas.



Modelled steady-state [^{3}CDOM] in the 1048 Swedish lakes under study*

References
1. *Analytical Chemistry*, 2011, *83*, 4614-4648.
2. *Chemistry - A European Journal*, 2014, *20*, 10590-10606.
3. *Chemical Reviews*, 2015, *115*, 13051-13092.
4. *Environmental Science: Processes and Impacts*, 2014, *16*, 732-740.
5. *Science of the Total Environment*, 2016, *541*, 247-256.
6. *Environmental Science & Technology*, 2015, *49*, 1646-1653.
7. *Chimia - International Journal for Chemistry*, 2007, *61*, 641-644.
8. *Global Change Biology*, 2011, *17*, 1186-1192.

Primary and Secondary Carbonaceous Species in PM10 and PM2.5 Samples

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Carbonaceous PM is composed of a refractory component, commonly called elemental carbon (EC), and an organic fraction, called organic carbon (OC). Organic aerosols represent a large fraction of atmospheric aerosols. The organic fraction can include saturated and unsaturated aliphatic compounds, aromatic compounds, alcohols, ketones, aldehydes, carboxylic acids, amines, sugars, polyols, and organic sulfur compounds[2]. Organic and elemental carbon were measured in daily PM10 and PM2.5 and 6 hours range time PM2.5 samples collected from September 2015 to October 2015 in a coastal rural site near Brindisi in the Apulia region (Italy), in order to determine factors affecting the carbonaceous aerosol variations. OC and EC were measured on Sunset Laboratory Thermal–Optical Carbon Aerosol analyser using NIOSH protocol.

Carbon content (total carbon TC) represented a considerable fraction for both PM10 and PM2.5. The highest values for both parameters were recorded when the winds blows from NE Europe and when Sharan Dust events have been recognized. The results show that OC and EC exhibited higher concentrations during the night hours, suggesting that stable atmosphere and lower mixing play important roles for the accumulation of air pollutants and hasten condensation or adsorption of volatile organic compounds.

Moreover, ATR-FTIR analysis were performed on some samples with the lowest and the highest OCsec and on samples characterized by Saharan Dust event. FTIR spectroscopy provides absorption peaks which can be identified and assigned to chemical bonds to identify functional groups in a complex sistem. The FTIR method is relatively simple and rapid and requires only small sample size. To our knowledge, there are only few examples of recent studies which are subjected to quantification or qualification of chemical species of aerosol samples. FTIR coupled with attenuated total reflectance (ATR) is a new technique developed recently. ATR FTIR analysis were carried out and it let identify organic functional groups included non-acid organic hydroxyl C-OH group (including sugars, anhydrosugars, and polyols, herein indicated as alcohol group), aromatic C=C-H group, aliphatic unsaturated C=C-H group, aliphatic saturated C-C-H group, non-acid carbonyl C=O group, carboxylic acid COOH group, and amine NH2 group. Among the inorganic ions, carbonates, sulfate, silicate and ammonium can be recognized.

References

1. Genga A., Ielpo P., Siciliano M., Siciliano T.; "Carbonaceous particles and aerosol mass closure in PM2.5 collected in a port city"; *Atmospheric Research*, 2017, *183*, 245-254.
2. Gilardoni, S., Liu, S., Takahama, S., M. Russell, L., Allan, J.D., Steinbrecher, R., Jimenez, J. L., De Carlo, P.F., Dunlea, E.J., Baumgardner D., "Characterization of organic ambient aerosol during MIRAGE 2006 on three platforms"; *Atmos. Chem. Phys.*, 2009, *9*, 5417–5432.

Cutting-edge developments in shotgun proteomics, peptidomics and shotgun phosphoproteomics in real matrices

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The keynote will give an overview of some applications of shotgun proteomics, and related technologies, in cutting-edge research fields. In particular, the potential of shotgun proteomics in shedding light on the interaction between nanomedicine vehicles and biological systems will be discussed. By studying the nature and composition of the proteins adsorbed onto such nanoparticles it becomes possible to understand the fate of the nanoparticles themselves and of their loaded drug, if the vehicles will reach the target cells or be cleared due to opsonization. Key case studies will be discussed, in particular to better understand the effect of a popular anti-opsonization strategy, i.e. PEGylation, and the use of model animal systems, such as mice, during nanomedicine vehicle development stages.

A brief overview of peptidomics will be provided. Initially considered a subfield of proteomics, peptidomics is demonstrating to be much more important than that, as an individual discipline to which ordinary proteomics technologies need to tailored for improved identification and to tackle common drawbacks due to endogenous peptide extraction, separation and unrestricted database search space; in particular, its potential in discovery of bioactive peptides from food and waste matrices will be considered.

Finally, the use of peptidomics in post-translational modification analysis will be discussed. General considerations on method development for phosphopeptide analysis will be presented, with a special attention to the investigation of complex real matrices and endogenous phosphopeptides characterization in samples of biological significance.

A New Magnetic Graphitized Carbon Black TiO2 Bomposite for Phosphopeptide Selective Enrichment in Shotgun Phosphoproteomics

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Protein phosphorylation is a dynamic and reversible post-translational modification that is widely used in biological sys-tems to regulate protein-protein interactions and thus, to rap-idly activate or deactivate signaling pathways. It has proven to play a key role in several biological processes, such as cellu-lar signaling and communication,1 cell adhesion and migra-tion, transcriptional and translational regulation, cell division and apoptosis.4 Gaining knowledge about these pathways is strongly related to cell activity and it may help shedding light on relevant physiological and pathological conditions. In this sense, proteomics technologies and mass spectrometry (MS) have become the leading tools for the study of transient post-translational modifications. However, despite the great poten-tial of HPLC-MS/MS in the field, direct analysis is generally not possible without prior enrichment of target proteins or peptides[1]. In this context, the development of new materials for use in phosphoproteomics is of great demand to fill the existing gaps and to allow for a comprehensive analysis. Popular methods for phosphopeptide enrichment consist of stationary phases in batch format, and self-made or commercial micro-columns packed into pipette tips. Some advantages over miniaturized column format can be found by using dispersive solid-phase magnetic separation. With respect to packed micro-columns, the use of magnetic phases avoids the step of column packing[2]. Graphitized carbon black (GCB) has been employed for extraction of several classes of analytes, due to the large surface area and the unique chemistry of its surface groups that allows to extract a wide range of analytes, including polar, acidic compounds. Despite the fact that structurally-related materials, such as graphene, found application as hybrid-components in phosphoproteomics, surprisingly, GCB has never been used for the selective enrichment of phosphopeptides. For this purpose, in the present work we used GCB to prepare a magnetic composite with TiO2 (mGCB@TiO2) that was then applied to yeast total extracts. We exploited the high surface area provided by nanostructures, the presence of nano-TiO2 for selective binding of phosphopeptides, and the magnetic responsiveness of magnetite for solid-phase separation. The material was extensively characterized at each modification step by transmission electron microscopy, Fourier-transformed infrared spectroscopy, thermogravimetric analysis, Raman spectros-copy and porosimetry. Next, the new system was applied for the enrichment of casein phosphopeptides from a simulated tryptic digest with bovine serum albumin (BSA:casein, 100:1). Finally, after assessing the potential applicability, the composite was em-ployed for enriching phosphopeptides from yeast protein digests. This allowed us not only to optimize the enrichment protocol, but also to fully compare its performance to commercial TiO2 spin columns. To achieve this aim, the optimized enrichment protocol was included in a typical shotgun proteomics analytical workflow based on nanoHPLC-MS/MS analysis.

References

1. Piovesana S., Capriotti A.L., Cavaliere C., Ferraris F., Iglesias D., Marchesan S., Laganà A.; "A New Magnetic Graphitized Carbon Black TiO_2 Composite for Phosphopeptide Selective Enrichment in Shotgun Phosphoproteomics"; *Anal. Chem.*, 2016, *88*, 12043-12050.
2. Ruprecht B., Koch H., Medard G., Mundt M., Kuster B., Lemeer S.; "Comprehensive and Reproducible Phosphopeptide Enrichment Using Iron Immobilized Metal Ion Affinity Chromatography (Fe-IMAC) Columns"; *Mol. Cell. Proteomics*, 2015, *14*, 205-215.

pH-Controlled Assembly of DNA Tiles

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We demonstrate a strategy to trigger and finely control the assembly of supramolecular DNA nanostructures with pH. Control is achieved via a rationally designed strand displacement circuit that responds to pH, and activates a downstream DNA tile self-assembly process. We observe that the DNA structures form under neutral/basic conditions, while the self-assembly process is suppressed under acidic conditions. The strategy presented here demonstrates a modular approach towards building systems capable of processing biochemical inputs and finely controlling the assembly of DNA-based nanostructures under isothermal conditions. In particular, the presented architecture is relevant for the development of complex DNA devices able to sense and respond to molecular markers associated with abnormal metabolism[1].

Reference
1. Webb B. A., Chimenti M., Jacobson M.P., Barber D. L.; *Nat. Rev. Cancer*, 2011, *11*, 671
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Comunicazioni Orali

A Validated SIM GC/MS Method for the Simultaneous Determination of Linear Polyalkylsiloxanes OH-*terminated* in Octamethylcyclotetrasiloxane

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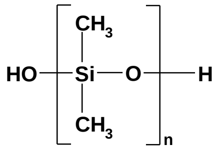
Optical fibers presently on the market are mainly manufactured by drawing from a cylindrical preform of silica[1]. Octamethylcyclotetrasiloxane ($[\text{-Si(CH}_3)_2\text{O-}]_4$) is the most commonly used liquid feedstock for high purity SiO_2 production performed at 180°C, according to the following reaction:

$$[\text{-Si(CH}_3)_2\text{O-}]_4 \; + \; 16\,O_2 \xrightarrow[180°\text{C}]{\Delta} 4\,SiO_2 \; + 8\,CO_2 \; + 12\,H_2O$$

Octamethylcyclotetrasiloxane feedstocks usually contain impurities deriving from the production process[2,3,4], as cyclic molecules possessing 3 to 8 silicon atoms and linear polyalkylsiloxanes OH-*terminated* (L_n, with $3 < n < 12$), having the formula:



$$HO\!\left[\!\begin{array}{c} CH_3 \\ | \\ Si\!-\!O \\ | \\ CH_3 \end{array}\!\right]_n\!H$$

In particular, linear polyalkylsiloxanes with $n > 6$, due to their high boiling point, form polymeric compounds[5], with consequent deleterious deposits in the vaporization and conversion equipment of the chemical plants[3].

In order to avoid serious problems to the silica glass manufacturing process and to maintain the fiber quality, the use of high purity siloxane feedstocks (total impurities < 0.25 *ppm*) is mandatory[3]. For this purpose, there are various processes that involve their purification[3,6]. To that end, the analytical determination of the high boiling impurities constitutes a crucial task.

In this communication will be discussed a new and high sensitive method to determine all the polyalkylsiloxanes OH-*terminated* contained in octamethylcyclotetrasiloxane feedstocks. Preconcentration and pretreatment, followed by mass spectrometric analysis in SIM mode, allowed the determination of these impurities with a detection limit of 50 *ppb*. The proposed method was applied to several octamethylcyclotetrasiloxane samples.

References
1. United States Patent N. 4,804,393, Yano *et al.*, 1989.
2. United States Patent N. 6,387,302 B1, Konya *et al.*, 2002.
3. United States Patent N. 5,879,649, Henderson *et al.*, 1999.
4. B. Hardman; "Silicones"; *Encycl. Polym. Sci. Eng.*, 1989, vol. 15, 204.
5. Nihan Nugay, Gabor Erdodi and J. P. Kennedy; *Journal of Polymer Science: Part A: Polymer Chemistry*, 2005, Vol. *43*, 630-637.
6. United States Patent N. 6,590,116 B1, Flynn *et al.*, 2003; United States Patent N. 4,156,689, Ashby *et al.*; 1979.

Identification of Urinary Biomarkers of Meat and Dairy Products Intake by Means of UHPLC-QTOF/MS Untargeted Metabolic Profiling

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Meat intake has been associated with positive as well as negative health outcomes. The nutritional importance of meat is related to the content of high quality proteins and other micronutrients essential for growth and development. On the other hand, red meat consumption has been associated to increased risk of colorectal cancer and, possibly, cardiovascular diseases, mortality and type 2 diabetes. However, a causal relation between red meat consumption and negative health outcomes is still controversial[1]. In order to shed light on this issue a reliable assessment of red meat intake is needed. Meat intake has often been assessed using 24-h recalls, weighed food diaries, and food frequency questionnaires[2], although they have been shown to be very imprecise methods[3]. Dietary biomarkers measured in biological fluids have been proposed as possible objective measurements of the actual intake of specific foods. Metabolomics offers a potential tool in the area of nutritional assessment[4] allowing measurement of a range of small molecules and identification of potential dietary biomarkers present in urine and blood. A meat intake marker should reflect dietary meat content and, at the same time, should be able to differentiate meat consumption from that of other protein-rich food such as dairy products. In this study, the identification of urinary meat and dairy exposure markers was accomplished after ingestion of red meat and dairy meals containing equal amounts of macronutrients. A randomized, controlled, cross-over single meal study was conducted in 17 subjects. In total, 48 hours urine samples were collected. This included urine samples collected 24 hours prior to ingestion of the test meal and urine samples collected during the first 2 hours, from 2 to 4 hours and from 4 to 24 hours after ingestion of the test meal. An ultra-high-performance-liquid chromatography coupled via electrospray (ESI) source to a Q-TOF mass spectrometer was used for separation and the metabolic profiling of the samples. To evaluate the effect of the meal over time on urine metabolome a linear mixed model was fitted for each detected feature. Twenty-four hours urine samples were analysed by multivariate data analysis by means of two different approaches: at first data were analysed by Partial Least Squares Regression (PLSDA), and subsequently data were investigated by multilevel-PLSDA to correct for the random effect of the subjects. The 78 compounds resulting significant for discriminating the two diets in both analysis have been selected as meat or dairy products intake biomarkers. The selected marker was fragmented to accomplish their chemical identification. Several markers for meat and dairy products intake were tentatively identified based on the accurate mass, fragmentation spectra and by means of comparison with available databases. Some of them were synthesized to allow the identity confirmation. Combinations of these markers are proposed as specific markers for meat or dairy product intake. However, further identity confirmation with authentic standard compounds and further validation in larger study settings are needed for several of the markers.

References
1. Klurfeld D. M.; *Meat Sci.*, 2015, *109*, 86-95.
2. Dragsted L. O.; *Meat Sci.*, 2010, *84*, 301-307.
3. Kipnis V., Midthune D., Freedman L., Bingham S., Day N.E., Riboli E., Ferrari P., Carroll R.J.; *Public Health Nutr.*, 2002, *5*, 915-923.
4. O'Sullivan A., Gibney M. J., Brennan L.; *Am. J. Clin. Nutr.*, 2011, *93*, 314-321.

On-line SPE-LC-MS/MS Analysis of Wide-Range Polarity Pharmaceutical Compounds in Aqueous Matrices: Problems and Solutions

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Modern environmental analytical chemistry must deal with the increasing demand of high-throughput analysis. Furthermore, the environmental monitoring of organic micropollutants in water samples is a fairly laborious issue, due to a number of reasons, such as the need of the simultaneous determination of a very high number of compounds, frequently characterized by a wide range of physicochemical properties and capable to exert negative effects on the environment, even at very low concentrations (i.e. parts per billion-trillion levels). All these issues can be faced using on-line solid phase extraction coupled to tandem mass spectrometric detection (on-line SPE-LC-MS/MS), which has been successfully applied to the monitoring of several classes of organic micropollutants in various aqueous matrices[1,2]. Pharmaceutical compounds in aqueous matrices are matter of environmental concern owing to their widespread use, continuous release, persistence, and increasing evidence for their ecotoxicological effects[3]. Pharmaceuticals are excreted either as such or as metabolites after human administration and via the sewage system they reach wastewater treatment plants (WWTPs)[4] where they are often inefficiently removed, thus being discharged into the receiving water bodies[5]. Pharmaceuticals represent a group of substances characterized by the presence of acid and/or basic functionalities and a very wide range of polarity, thus representing a challenge for the analytical chemist when a multiresidual determination is required. In this work, the applicability of the on-line SPE-LC-MS/MS approach to the determination of a number of pharmaceutical compounds characterized by very different physicochemical properties was investigated. Antibiotics, beta-blockers and anti-inflammatory drugs most used in Italy were selected according to the reports of the Italian Medicine Agency, together with some metabolites. Different SPE sorbents, such as the poly(divinylbenzene-co-N-vinylpyrrolidone) (PVB-VP) and PVB-VP functionalized with a weak cation exchange group, and stationary phases (e.g. octadecylsilane and pentafluorophenyl silane) were tested. Under the best experimental conditions, recoveries included in between 40 and 120% were obtained on MilliQ water. Apparent recoveries significantly differed from these values, mainly due to matrix effects within the ionization process. Detection limits were however included from sub-ng/L to tens of ng/L, depending on the compound and sample analysed. The overall analysis time per sample was about 25 minutes. The analysis of various effluent WWTP samples evidenced the presence of several pharmaceuticals and especially antibiotics and beta-blockers, at concentrations as high as tens of µg per litre.

References

1. L. Ciofi, D. Fibbi, U. Chiuminatto, E. Coppini, L. Checchini, M. Del Bubba; "Fully-automated On-line Solid Phase Extraction Coupled to High-Performance Liquid Chromatography-Tandem Mass Spectrometric Analysis at sub-ng/L Levels of Selected Estrogens in Surface Water and Wastewater"; *Journal of Chromatography A*, 2013, *1283*, 53-61.
2. L. Ciofi, C. Ancillotti, U. Chiuminatto, D. Fibbi, B. Pasquini, M.C. Bruzzoniti, L. Rivoira, M. Del Bubba; "Fully-automated On-line Solid Phase Extraction Coupled to Liquid Chromatography-Tandem Mass Spectrometry for the Simultaneous Analysis of Alkylphenol Polyethoxylates and Their Carboxylic and Phenolic Metabolites in Wastewater Samples"; *Analytical and Bioanalytical Chemistry*, 2016, *408*, 3331-3347.
3. K. Fent, A.A. Weston, D. Caminada; "Ecotoxicology of human pharmaceuticals"; *Aquat. Toxicol.*, 2006, *76*, 122-159.
4. D. Rossini, L. Ciofi, C. Ancillotti, L. Checchini, M.C. Bruzzoniti, L. Rivoira, D. Fibbi, S. Orlandini, M. Del Bubba; "Innovative Combination of QuEChERS Extraction with On-line Solid-Phase Extract Purification and Pre-Concentration, Followed by Liquid Chromatography-Tandem Mass Spectrometry for the Determination of Non-Steroidal Anti-Inflammatory Drugs and Their Metabolites in Sewage Sludge"; *Analytica Chimica Acta*, 2016, *935,* 269-281.
5. D.S. Aga; "Fate of Pharmaceuticals in the Environment and in Water Treatment Systems"; 2008, CRC Press, Boca Raton, FL.

Insights into Structure-Bioaccessibility Relationships of Polyphenols in Red Chicory by HPLC-MS/MS

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Two varieties of red chicory from southern Po Delta area have been characterized in terms of polyphenols content. Attention has been mostly paid to phenolic acids and flavonoids[1]. Qualitative and quantitative determinations have been performed on sample extracts by HPLC-MS/MS. Both glycosylated and ester forms of phenolic acids as well as glycosylated flavonoids were mainly identified. Seven target bioactive compounds were selected and their bioaccessibility from red chicory vegetable matrix was investigated through simulated in-vitro static digestion process[2,3]. This gastro-intestinal model uses simulated fluids (i.e., salivary, gastric and duodenal) based on electrolytic solutions of different physiological enzymes miming the stages of digestion process. Fractions of polyphenols released from the vegetable matrix were quantitatively determined. Bioaccessibility results show well defined behaviors associated with both specific structures of aglycone or phenolic acid and position of O-glycosyl moiety. Dicaffeoyltartaric acid together with apigenin-7-O-glucoside and kaempferol-7-O-glucoside have similar bioaccessibility trend that is characterized by a higher value for duodenal phase than for gastric one. Quercetin-3-O-(6"-O-malonyl)-glucoside behave in reverse way and gastric bioaccessibility turns higher than duodenal. Lastly, the difference between gastric and duodenal bioaccessibility is ehnanced in the case of cyanidin-3-O-glucoside and two isomers of caffeoylquinic acid. Advanced investigations involved also living biological systems (i.e., cellular lines) and they were aimed at understanding effects of polyphenols on degenerative diseases. Particularly, investigation of the role of polyphenol metabolites and their positive synergic effects together with other nutraceutics was promising for uncovering hidden aspects of bioactives mode of action and their health effects.

References
1. C. Carazzone, D. Mascherpa, G. Gazzani, A. Papetti; *Food Chemistry*, 2013, *138*, 1062-1071.
2. F. Saura-Calixto, J. Serrano, I. Goni; *Food Chemistry*, 2007, *101*, 492-501.
3. M. Minekus, in “The impact of food bioactives on gut health: in vitro and ex vivo models”, Springer (New York), 37-46.

Shotgun Proteomics for Detecting Seafood Fraud

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Nowadays, there is an increasing interest on food safety and, in consequence, fighting food fraud has become very important. The development of new analytical technologies, as well as the application of the existing ones, can be very helpful to detect fraud in the seafood commerce. In particular, the discrimination between fresh and frozen-thawed seafood is very important to protect consumers. The selling of frozen-thawed fish labeled as fresh it also represents a potential risk for the consumer's health related to microbiological safety: when freezing-thawing cycle are repeated, it leads the activation of residing dormant micro flora increasing the total microbial count.

In this research, we employed a shotgun proteomic approach for the detection of seafood fraud. A new experimental protocol was developed for the extraction of proteins from tissue samples of curled octopus (Eledone cirrhosa). Through the use of the high-resolution LC-MS/MS for the reliable and fast quantitation of proteins, we were able to identify new biomarkers for the differentiation between fresh and frozen-thawed octopus.

In conclusion, we demonstrated that shotgun proteomics could have a great impact on the rapid screening of seafood safety.

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In Vitro Meningeal Permeation of $MnFe_2O_4$ Nanoparticles

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$MnFe_2O_4$ nanoparticles (NPs) are commonly produced in some occupational settings and may reach high concentration in activities such as arc-welding or ferroalloy metallurgy. Manganese is an essential cofactor in enzyme activities but it has been demonstrated that long-term exposure to excessive levels can lead to "manganism", a neurodegenerative disease resembling Parkinson features[1]. The same symptoms have been described in rats exposed to MnO_2 NPs[2]. Inhaled NPs deposit partially in pharynx and nasopharynx and may reach the central nervous system through the olfactory nerve, which is completely enveloped by the meningeal membranes throughout its course from the nasal cavity to the olfactory bulb. The aim of the present study was to assess the permeability properties of meningeal membranes, currently undefined, towards $MnFe_2O_4$ NPs, which represent a common by products in the arch-welding fumes[3] and may exert chronic neurotoxic effects on humans.

This study investigated in vitro the transmeningeal absorption of 50 nm $MnFe_2O_4$ NPs, using excised porcine meninges mounted on Franz diffusion cells. Two donor solutions have been tested: the first containing $MnFe_2O_4$ NPs (2.0 g/L) and the second obtained by the ultrafiltration of the first one with centrifugal ultrafilter (MWCO 10 kDa), in order to test only the NPs water soluble fraction[4]. At selected intervals 1 mL of the receiving bathing solution was withdrawn and collected for the analysis, and immediately replaced with an equal volume of fresh made physiological solution. At the end of the experiment the meninges pieces were removed, washed and mineralized for the following analysis. Each experiment was carried separately for 4 hours. Inductive Coupled Plasma Mass Spectrometry was used to determine the total manganese and iron concentrations in the receivingphases (ion mass selected: 55 u.m.a. for Mn and 54 and 57 u.m.a. for Fe). ^{103}Rh has been used as internal standard for all the samples. The analysis was carried out in kinetic energy discrimination (KED) mode. The total iron and manganese concentrations in the donor phases and in the solutions resulting from the tissue mineralization were performed by Inductive Coupled Plasma – Optical Emission Spectrometry. The measurements were conducted at the operative wavelengths of 238.204 nm for Fe and 257.610 nm for Mn. Results (expressed as mean and SD) showed that Mn flux permeation through the meninges could not be calculated, since only trace of the metal was found in receiving solutions of cells exposed to $MnFe_2O_4$ NPs (5.5 ± 4.4 ng/cm^2), ultrafiltered solution (3.5 ± 3.2 ng/cm^2) and blank cells (2.1 ± 1.2 ng/cm^2). Differences did not reach the statistical significance.

This study shows that $MnFe_2O_4$NPs penetrate the meningeal membrane in a non-significant amount, thus making unlikely the hypothesis of a transcellular and paracellular absorption through the olfactory nerve but but not excluding the hypothesis of an intraneuronal absorption.

References

1. Ellingsen D.G., Konstantinov R., Bast-Pettersen R., Merkurjeva L., Chashchin M., Thomassen Y., Chashchin V.; "A Neurobehavioral Study of Current and Former Welders Exposed to Manganese"; *Neurotoxicology*, 2008, *29*, 48-59.
2. Li T., Shi T., Li X., Zeng S., Yin L., Pu Y.; "Effects of Nano-MnO_2 on Dopaminergic Neurons and the Spatial Learning Capability of Rats"; *Int. J. Environ. Res. Public Health*, 2014, *11*, 7918-7930.
3. Andujar P., Simon-Deckers A., Galateau-Sallé F., Fayard B., Beaune G., Clin B., Billon-Galland M.A., Durupthy O., Pairon J.C., Doucet J., Boczkowski J., Lanone S.; "Role of Metal Oxide Nanoparticles in Histopathological Changes Observed in the Lung of Welders"; *Part Fibre Toxicol.*, 2014, *11*, 23.
4. Mauro M., Crosera M., Bovenzi M., Adami G., Filon F.L.; "Pilot Study on in Vitro Silver Nanoparticles Permeation Through Meningeal Membrane"; *Colloids Surf B Biointerfaces*, 2016, *146*, 245-9.

Identification of MT-45 Metabolites: *in silico* Prediction, *in vitro* Incubation with Rat Hepatocytes and *in vivo* Confirmation

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The new psychoactive substances (NPS) do not represent a novelty in the drug market anymore, in fact the phenomenon has been largely reported and monitored worldwide since the late nineties[1]. The use of these substances is associated with dissociate mental states and psychedelic sensations; however because of the lack of legal restrictions to their marketing, these drugs are easily available. These pharmacological effects and the difficulty in detecting the parent compound in urine, highlight the importance of metabolite identification for developing analytical methods for clinical and forensic investigations. The aim of this work was to ascertain the chemical structures of the metabolites of MT-45, in order to allow further pharmacological studies and to better assess the health implications of the abuse of this substance[2]. MT-45 is a synthetic opioid firstly developed in the early 1970s by the Japanese company Dainippon Pharmaceutical Co. Ltd, it has a pharmacological activity comparable to morphine and it has been involved in intoxications and fatalities reported in Europe and in USA[3]. It was recently subjected to control measures, but until now, the metabolic pathways of the substance were still unknown[4]. When metabolism is unknown, determining targets for analysis is critical, but using rat hepatocytes and LC–HRMS, 14 novel phases I and II MT-45 metabolites were identified: products of monohydroxylation, dihydroxylation, and N-dealkylation; glucuronide conjugation of mono- and dihydroxylated metabolites as suggest before by Scheidweiler et al for several synthetic cannabinoids[5]. The detected metabolites were firstly predicted *in silico*, then incubation of the drug with rat hepatocytes was carried out and the obtained metabolites were identified by LC–HRMS, with retention times, mass shift between theoretical mass and observed mass (<10 ppm), peak abundance and fragmentation pattern. Hydroxylated MT-45 was found to be the major metabolite of MT-45 *in vitro* experiments. The presence of all metabolites was confirmed by *in vivo* experiments in urine samples of CD-1 male mice; in these samples hydroxy-MT-45 glucuronide and di-hydroxy-MT-45 glucuronide are the most abundant metabolites, while the parent drug is found at concentration < 10 ng mL^{-1} after 300 min. The knowledge of phase I and II MT-45 metabolite structure is then crucial to develop analytical methods to identify MT-45 consumption in clinical and forensic testing.

References
1. King L.A. and Kicman A.T.; "A Brief History of 'new psychoactive substances' "; *Drug Testing and Analysis*, 2011, *3*, 401-403.
2. Papsun D., Krywanczyk A., Vose J.C., Bundock E.A., Logan B.K.; *Journal of Analytical Toxicology*, 2016, *40*, 313-317.
3. European Monitoring Centre for Drugs and Drugs Addiction, 2015; avaible at: http://www.emcdda.europa.eu/attachements.cfm/att_233323_EN_MT-45%20Risk%20Assessment%20Report.pdf.
4. World Health Organization, 2015;. avaible at: http://www.who.int/medicines/access/controlled-substances/5.1_MT-45_PR1.pdf?ua=1.
5. Scheidweiler K.B., Jarvis M.J., Huestis M.A.; *Anal. Bioanal. Chem.*, 2015, *407*(3), 883-897.

All PEDOT:PSS Electrochemical Transistors as a Platform for Sensing

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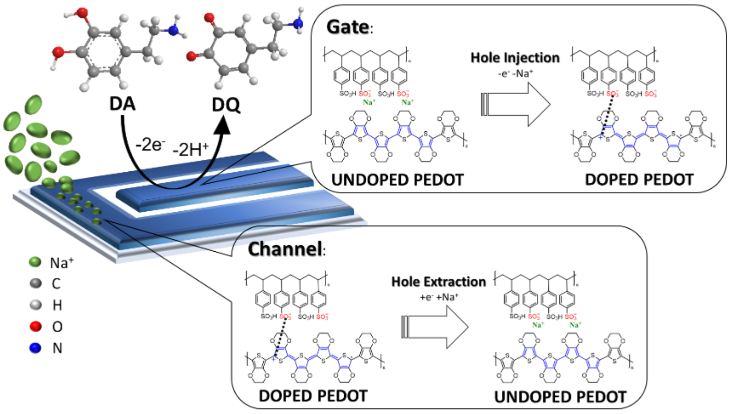
Organic electrochemical transistors (OECTs) are devices which find growing interest in the field of biological and chemical sensing. Although the OECT transduction is based on electrochemical reactions, the transistor architecture offers several advantages respect to amperometric sensors such as signal amplification, the use of an easy and cheap readout electronics, low supply voltage (usually < 1 V), low power operation (< 100 μW), bio-compatibly and, moreover, they can be easily miniaturized and adapted to non-flat, flexible and even textile devices[1]. This contribution want to report the potentiality of such devices by describing an OECT based only on PEDOT:PSS as conductive material, that can be exploited to obtain low cost sensors[2,3] with very high performance.
The sensor was optimized by studying the response to different redox compounds of biological interest such as ascorbic acid, dopamine, adrenaline and uric acid. The bio-molecules react with PEDOT:PSS by extracting charge carriers from the transistor channel, and consequently an increase of analyte concentration leads to a decrease of the absolute value of the drain current.



The main drawback of such devices is the lack of selectivity which hinders its wide use in real applications. To address this issue, we use a dual approach: on one side we have implemented a potentiodynamic approach that exploits the variation of the operating gate bias voltage in order to obtain a trans-conductance curve wherein the waves due to different redox compounds are separated. On the other side, the physical and chemical modification of the PEDOT lactice of the gate electrode offers great opportunities for the implementation of a selective sensor.

References
1. I. Gualandi, M. Marzocchi, A. Achilli, D. Cavedale, A. Bonfiglio, B. Fraboni; *Scientific Reports*, 2016, *6*, 33637.
2. I. Gualandi, M. Marzocchi, E. Scavetta, M. Calienni, A. Bonfiglio, B. Fraboni; *J. Mater. Chem. B*, 2015, *3*, 6753-6762.
3. I. Gualandi, D. Tonelli, F. Mariani, E. Scavetta, M. Marzocchi, B. Fraboni; *Scientific Reports*, 2016, *6*, 35419.

Development of enzyme-based microsensors for *ex vivo* analyses

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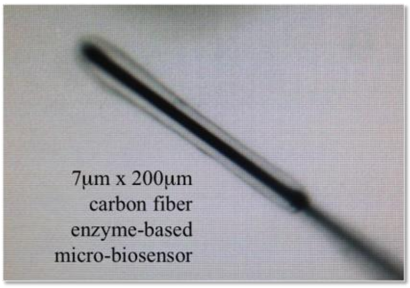
Nowadays real-time quantitative measurements of many proteins, metabolites and cancer biomarkers, are feasible by the use of biosensors for *in vitro* and *in/ex vivo* studies[1]. Although, strategies on biosensor design are rapidly increasing, enzymatic biosensors remain a large and important field of study. Enzymes achieve molecular recognition of the substrate based on structural complementarity and exploit an analyte-dependent step to convert an electrochemically inert substrate to an active product, often revealing high selectivity, sensitivity, time scale and information content. Even if, amperometric biosensors have been around since the early 1960s[2,3], it is the production of very tiny micro-electrode biosensors that offers great utility for studying chemical signalling for *in vitro* (at single cell level) and *in/ex vivo* studies. These microelectrode biosensors have the advantage of offering a better spatial and temporal resolution and they are considerably less invasive than other electrode (i.e. microdialysis electrodes)[4]. The miniaturization of biosensors is challenging, as they need to be both extremely small and highly sensitive. In fact, smaller is the sensor, smaller is the electrode surface area, and consequently the recorded amperometric signal diminishes[1]. The requirement in miniaturizing biosensors is to maintain a signal to noise ratio that enables effective and sensitive detection of the analyte. The tiny sensing surface of the sensor has to be coated with a high density of enzymes in their native active conformation. Furthermore, for *ex vivo* analyses, it is mandatory to control the selectivity of the signal and the mechanical strength of the sensor itself, which has to enter in tissues without damaging.

In this work, we present the development of small, robust and highly active micro-electrode enzymatic biosensors for detecting metabolites as glucose, lactate and ATP from single living cells to tissues analysis., *such*



References
1. N. Dale et *al*.; *TRENDS in Biotechnology*, 2005, *23* (8), 420-428.
2. J. Wang; *Electroanal.*, 2001, *13*, 983-988.
3. L.C. Clarck Jr.; *Biosens. Bioelectron.*, 1993, *8*, iii-vii.
4. A.S. Khan, A.C. Michael; *Trends Anal. Chem.*, 2003, *22*, 503-508
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Potential and Limitations of Voltammetric Measurements for the Characterization of Electrode Surface

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In this work, we tested the possibility to use voltammetry for the evaluation of the area of solid electrodes. In the first step of the research study we adopted two voltammetric techniques, well known in the literature: i) cyclic voltammetry (CV) at different scan rates, followed by processing of the peak height with the Randles-Sevcik equation; ii) linear sweep voltammetry (LSV) at different electrode rotation rates, followed by data treatment with Levich equation[1,2]. The ferrocene/ferrocenium redox system was chosen as a probe for its well-known reversible process of diffusion-controlled single electron transfer. Acetonitrile and tetrabutylammonium esafluorophosphate were used as solvent and supporting electrolyte respectively. Initially attention was focused on a solid gold electrode (SGE). The evaluation of its area was made both on the electrode as received, without applying any treatment, and after a drastic surface treatment, to compare the effect of mechanical polishing on the measured area. The results obtained showed that such a treatment gave rise to a significant decrease of the standard deviation of the results and a decrease of the value measured for the area. Method i) was then applied to a glassy carbon electrode (GCE) in three different conditions: unmodified and modified with an Au-film (AuF-GCE) and with an Au-nanoparticle layer (AuNP-GCE), to investigate the influence of the “roughness” of the electrode surface on the value measured for the area. According to the literature, the above-mentioned electrochemical techniques should respond to the electrode projected areas[2,3]: however, we found that the measured areas differ for each modification, suggesting that the morphology of the active surface influences the results of the calculation. Subsequently, method i) was applied to home-made carbon paste electrodes (CPE) of different sizes, to test the relationship between the diameter of the electrode body and the measured area. The calculated areas were compared with those obtained by recording electrode images by scanning electron microscopy (SEM) and processing the data with Wolfram Mathematica software. In the second step of the study, the actual active surfaces of the SGE and of the two Au-modified GCEs were estimated by CV in H_2SO_4, from the areas of the cathodic peak obtained in each voltammogram, through the theoretical charge associated with the reduction of the oxide layer per unit surface area of gold[4]. In conclusion, voltammetry provides information on the area of solid electrodes, but, despite the notoriety of the equations considered in this study, there are some doubts about the kind of “area” actually involved in the measurement process; further studies are required to correctly interpret experimental results. Finally, the evolution of the SGE surface during an extended period of usage was checked by periodically recording cyclic voltammograms in H_2SO_4. Clear differences were observed in the CV curves over time and a relationship between the shapes of the voltammograms and the performance of the electrode was found: therefore, CV can be a used to monitor the state of the SGE surface and identify the need for a mechanical polishing or even a substitution of the electrode.

References
1. Brown R. J. C. and Milton M.J.T.; *IEEE Transactions on Instrumentation and Measurement*, 2007, *56*, 280-283.
2. Bard A. J. and Faulkner, L.R.; “Electrochemical Methods. Fundamentals and Applications”, 2° Edition, J. Wiley & Sons, New York, 2001.
3. Neghmouche N. S. and Lanez T.; *Recent Trends in Physical Chemistry an International Journal*, 2013, *1*, 1-3.
4. U. Oesch and J. Janata; *Electrochimica Acta*, 1983, *28*, 1247-1253.

Development of an Electrochemical Magneto-Immunosensor for the Detection of *Campylobacter*: A Preliminary Study

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Campylobacter is an important pathogen genus that cause acute bacterial diseases in humans worldwide. Most infections (about 90%) are caused by *C. jejuni* species, less frequent are those caused by *C. coli*, while sporadic cases are caused by *C. lari* species and *C. upsaliensis*. Outbreaks of Campylobacteriosis have traditionally been linked to the consumption of food products of animal origin (e.g. meat and eggs) but, more recently, an increasing number of outbreaks have been associated to contaminated fruits and vegetables, especially raw leafy green vegetables[1]. Conventional bacterial testing methods rely on specific microbiological media to isolate and enumerate viable bacterial cells in food. These traditional methods are very sensitive and inexpensive, but require several days to generate results because they rely on the ability of microorganisms to multiply to produce visible colonies. Therefore, rapid, sensitive and specific methods to detect pathogens are needed. In this work a sandwich ELIME (Enzyme-Linked Immuno Magnetic Electrochemical) assay to detect *Campylobacter* is reported. The proposed system is similar to that already developed by our research group for *Salmonella enterica*[2,3]. Magnetic beads (MBs), coupled to a strip of eight-magnetized screen-printed electrodes, effectively supported a sandwich immunological chain. Enzymatic by-product is quickly measured by differential pulse voltammetry, using a portable instrument. Different antibodies, blocking agents and treatments for bacterial cultures were tested. The final system employs: MBs tosyl-activated blocked with dry milk and coated with a capture polyclonal antibody anti-*Campylobacter*, whole *Campylobacter* cells (inactivated with NaN_3) and a detection antibody conjugates with ALP enzyme. For a simple and rapid assay, the coating and blocking steps were performed in a preliminary phase, while the two sequential incubations for the immuno-recognition events were merged in a single step of 1 h. The final proposed conditions are those that ensured the best analytical performance for *C. coli*, while, to date, there are still difficulties to detect *C. jejuni*. The future work will focus on improving the response towards *C. jejuni* and the next application of the assay in contaminated matrices, such as irrigation water and vegetables, object of various community alerts in the last few years.

References
1. S. Park, B. Szonyi, R. Gautam, K. Nightingale, J. Anciso, R. Ivanek; "Risk Factors for Microbial Contamination in Fruits and Vegetables at the Preharvest Level: A Systematic Review"; *J. Food Prot*., 2012, *75*, 2055-2081.
2. G. Volpe, E. Delibato, L. Fabiani, E. Pucci, S. Piermarini, A. D'Angelo, F. Capuano, D. De Medici, G. Palleschi; "Development and Evaluation of an ELIME Assay to Reveal the Presence of Salmonella in Irrigation Water: Comparison with Real-Time PCR and the Standard Culture Method"; *Talanta*, 2016, *149*, 202-210.
3. L. Fabiani, E. Pucci, E. Delibato, G. Volpe, S. Piermarini, D. De Medici, G. Palleschi, F. Capuano; "ELIME Assay vs Real-Time PCR and Conventional Culture Method for an Effective Detection of Salmonella in Fresh Leafy Green Vegetables"; *Talanta*, 2017, *166*, 321-327.

Silica-Based Composites for the Consolidation of Earthen Materials

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Earthen materials are largely used in the architecture of many areas of the world, but the lack of well-established processing techniques and recipes make their conservation challenging. The object of this research is to develop a compatible and long-lasting consolidating treatment for adobe bricks, unbaked mixtures of soil and water, often added with organic matter and/or lime. We are experimenting the formulation and application of a silica-based system, where the combination with a cellulosic derivative and nano-lime aims at obtaining greater effectiveness and compatibility with the substrate.
Mesoporous silica nanoparticles were prepared following a synthesis[1] selected to obtain adequate particle size and porosity (250 nm uniform spheres with 300-600 m^2/g BET surface area were observed with SEM, DLS and porosimetry). Various amounts of *Klucel*®-G (hydroxypropyl cellulose ethanol solution) and *NanorestorePlus*® ($Ca(OH)_2$ nanoparticles ethanol dispersion) were added to the silica aqueous dispersion and kept under stirring to maximize the interaction. Components proportions were chosen according to common restoration applications and in order to minimize the aqueous content. The systems obtained were characterized by DLS, Z Potential, turbidimetry, TGA, FT-IR and SEM-EDS.
Turbidimetric tests confirmed the expected stabilizing effect of hydroxypropyl cellulose on silica, while almost instantaneous flocculation occurs in $Ca(OH)_2$-silica systems, in accordance with surface charge measures. Interestingly, the ternary system maintains a significant stability over several days. FT-IR analyses pointed out an intensification of the stretching band at 965 cm^{-1}, characteristic of calcium silicate hydrate[2,3], in all the systems containing silica and $Ca(OH)_2$ nanoparticles. The hypothesis of the formation of a cementing phase is supported by SEM observations of similar structures. Further analyses are underway. Following these first results, one of the ternary formulations was selected for preliminary application tests on adobe samples from Mexico.

References
1. Z. Gao, I. Zharov; "Large Pore Mesoporous Silica Nanoparticles by Templating with a Nonsurfactant Molecule, Tannic Acid"; *Chem. Mater.*, 2014, *26*, 2030–2037.
2. P. Yu, R. Kirkpatrick, B. Poe, P. F. McMillan, X. Cong; "Structure of calcium silicate hydrate (C-S-H): Near-, Mid-, and Far-Infrared Spectroscopy"; *J. Am. Ceram. Soc.*, 1999, *82* [3], 742–48.
3. K. Baltakys, R. Jauberthie, R. Siauciunas, R. Kaminskas; "Influence of Modification of SiO2 on the Formation of Calcium Silicate Hydrate"; *Materials Science-Poland*, 2007, Vol. 25, No. 3.

Chemical Poly Ethyl Methacrylate (PEMA) Organogels for the Removal of Pressure Sensitive Tapes (PSTs) from Paper Artworks

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Chemical poly ethyl methacrylate (PEMA) organogels loaded with Diethyl Carbonate (DEC) were synthesized by means of radical polymerization[1,2]. These systems are specifically designed for the removal of degraded Pressure Sensitive Tapes (PSTs) from paper artworks, a very common issue in the field of manuscripts and drawings restoration. DEC, an organic green solvent, shows interesting swelling properties towards PSTs components; besides it is inert to most common inks and dyes, unlike other commonly used cleaning systems such as polar solvents and microemulsions[3].

Several organogels were obtained by changing reaction parameters; on the basis of macroscopic evaluations (e.g. mechanical properties, homogeneity), some systems were chosen for a deep physico-chemical characterization performed by means of different techniques. Thermogravimetry (DTG), Differential Scanning Calorimetry (DSC), and gravimetric analysis were used to assess solvent content and uptake/release behaviour of gels; rheological analysis permitted the evaluation of their viscoelastic properties; Fourier Transform Infrared Spectroscopy (FT-IR) and Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) allowed to investigate the presence of unwanted residues in the exchange solvents and the effectiveness in the removal of PSTs. The penetration of DEC through the backing layer of PSTs and the swelling of the adhesive was investigated by means of Laser Scanning Confocal Microscopy (LSCM).

Cleaning tests on mock-up samples and real artworks were also successfully performed.

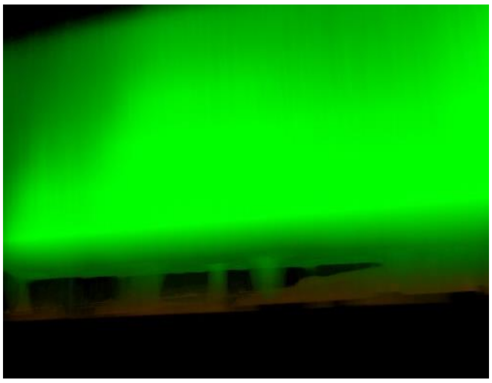

Fig. 1 – Laser Confocal image of a PEMA-DEC gel onto a PST sample: penetration of DEC (in green) through the backing up to the adhesive layer (in red)

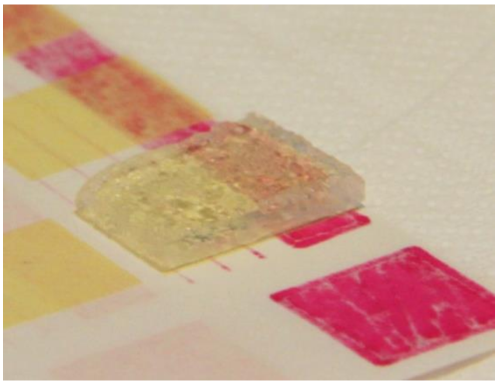

Fig. 2 – Application of a PEMA-DEC organogel for the removal of a Masking Tape from a mock-up sample

References
1. M. D. Pianorsi, M. Raudino, N. Bonelli, D. Chelazzi, R. Giorgi, E. Fratini, P. Baglioni; *Pure Appl. Chem.*, 2017.
2. K. K. Chee; *Polymer Gels and Networks*, 1997, *5*, 95-104.
3. F. Mizia, M. Notari, F. Rivetti, U. Romano, C. Zecchini; Chimica & Industria - April 2001.

Surface Cleaning of Artworks: Structure and Dynamics of Nanostructured Fluids Confined in a Polymeric Network

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Nanosystems and confinement tools for the controlled release of a cleaning agent, e.g., hydrogels and microemulsions, have been used for several years for the treatment of delicate surfaces in art restoration interventions. However, notwithstanding the unprecedented achievements from an applicative point of view, a fundamental comprehension of their interaction mechanism is still lacking. In this study PVA hydrogels, obtained via freeze-thaw processes, are prepared as scaffolds for water-based nanostructured fluids for application in the cleaning of artworks: rheological, thermal, microscopic and scattering techniques showed that, depending on the number of freeze-thaw cycles, the hydrogels exhibit different physicochemical and viscoelastic properties, making them suitable for application in a broad range of cleaning issues. The gels have been loaded with an oil-in-water microemulsion and the diffusion of the microemulsion droplets inside the polymeric network has been investigated through Fluorescence Correlation Spectroscopy (FCS), demonstrating that the microemulsion is permanently kept inside the matrix and can freely diffuse in the network. In addition, we show that, when the gel-microemulsion system is put in contact with a layer of hydrophobic grime, a dynamic interaction between the microemulsion droplets and the underlying layer is established, leading to the solubilization of the hydrophobic molecules inside the droplets in the gel matrix. Thus, for the first time, through FCS, insights about the removal mechanism of hydrophobic grime upon interaction with cleaning agent embedded in the polymeric matrix, are obtained. Some examples of significant case studies treated with these innovative materials will be presented.

Nanocomposites for the Consolidation and Deacidification of Cellulose-Based Artifacts

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A restoration method designed for the conservation of degraded fibrous-based artifacts should addressed the two main problems concerning these materials. Firstly, a mechanical reinforcement of artifacts is usually needed to ensure that the original material keeps its integrity. Moreover, pH buffering is required to prevent acidic degradation that is inherent to natural materials[1].
It has been recently shown that these two issues are related. For instance, it takes less than 100 years for acidic compounds to induce a significant loss of mechanical properties in canvases based on natural materials. (2) The same degradation effect of acidic compounds is found in paper-based artworks, drawings and documents. In this regard, several deacidification methods have been proposed and proven efficient in hampering the degradation of cellulose[3,4,5].

Research efforts have been recently devoted to the development of a nanocomposite material for the consolidation and concomitant pH adjustment of cellulosic works of art and artifacts that is one of the goal within the EU Project NANORESTART.
The use of nanocellulose, in combination with nanoparticles and cellulose derivatives, could ensure the consolidation of fiber-based materials using almost entirely natural materials. The choice of these materials is due to the high compatibility of the proposed treatments with the original fibrous support, which is essential from the conservation point of view.
Considering the high variability of cellulose-based artifacts, several different approaches were followed in order to provide conservators with a wide palette of tools that can be used on different works of art that are in need of both consolidation and deacidification treatments.
Nanocomposite materials were analyzed in order to gain more information about their structure and characteristics. Mechanical tests on not aged and aged reference samples were used to assess the consolidation efficacy of the proposed consolidation treatments before testing on real case studies.

References
1. J. W. Baty, C. L. Maitland, W. Minter, M. A. Hubbe and S. K. Jordan-Mowery; *BioResources*, 2010, *5*, 1955.
2. M. Oriola, A. Možir, P. Garside, G. Campo, A. Nualart-Torroja, I. Civil, M. Odlyha, M. Cassar, M. Strlic; *Anal. Meth.*, 2014, *6*, 86-96.
3. R. Giorgi, L. Dei, C. Schettino and P. Baglioni, in Prepr. IIC Balt. Congr. 2002, Work. Art Pap. Books, Doc. Photogr. Tech. Conserv., edited by V. Daniels, A. Donnithorne, and P. Smith (International Institute for Conservation, Baltimore, 2002), pp. 69–73.
4. G. Poggi, R. Giorgi, N. Toccafondi, V. Katzur and P. Baglioni; Langmuir 2010, *26*, 19084.
5. G. Poggi, N. Toccafondi, L. N. Melita, J. C. Knowles, L. Bozec, R. Giorgi and P. Baglioni; *Appl. Phys. A*, 2014, *114*, 685.

FIB-FESEM-EDX Study of Silver Roman Coins: Characterization Of The Core Microstructure And Corrosion Products With A Multi-Analytical Approach

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Metal artifacts are among the most common materials in the Cultural Heritage field: alloys have been used in several fields of everyday life and their analysis can prove useful information about the technology of the ancient populations. In particular, coins are important for studying provenance, dating, minting and corrosion processes as well as provenance and stratigraphy of the archaeological sites[1,2].

In this work a set of Roman silver coins, dated back to the Antonini's period, has been analyzed using FIB-FESEM-EDX aiming to establish the used technique for the silvering and discriminating different mints. Recently, this approach was used as a complementary technique for the characterization of bronze coins[3] but this is the first application on Roman silver coins. The aim of this work is to investigate the microstructure and the composition of the alloy with a micro-invasive approach. Commonly to investigate the composition of the metal core are used invasive and destructive techniques, therefore the developing of methods with minimal damage on metal is of a great interest.

The study of Antonini's coins is also important as in that historical period Roman Empire underwent to a severe debasement which influenced coinage, so the surface silvering it is still an open question. Diocletian in the 294 A.D. introduced a complex alloy (Cu-Sn-Pb-Ag) with an Ag-rich surface patina of 2 µm. Some coins of the set show a very fine silvered surface with a core composition entirely made of Cu, whereas others have the composition made of Sn-Cu-Pb with a very low concentration of Ag. This technique has been joined with surface analysis (Raman spectroscopy, SEM mapping, voltammetry of microparticles (VMP) and electrochemical impedance spectroscopy (EIS)) for a deeper knowledge of the samples. The results showed the leaching of the Sn and Pb as well as of the Cu that formed several common products on the surface of the coins, *i.e*, Cu_2O, CuO, PbO, SnO. The presence of AgCl has been detected in several coins.

In conclusion, FIB-FESEM-EDX analysis provides information about the composition, structure and thickness of the metal patina as well as the composition and microstructure of the metallic core which in turn reflects the technology of minting. As a result, FIB-FESEM-EDX features yield information for the diagnostic, authentication, technologies and historical context in which the coins were fabricated. Such multi-analytical data allow us the possibility of screening the coins minting, obtaining significant differences between those minted in Roma and those minted in the Gallia.

References
1. Domènech, A. et *al.*, *Electroanalysis*, 2011, *23*(12), pp.2803–2812.
2. Di Turo, F. et *al.*; *Analytica Chimica Acta*, 2017, *955*, pp.36-47.
3. Doménech-Carbó, A. et al., *Talanta*, 2017, *169*, pp.50–56.

I Materiali E La Tecnica Pittorica Di Konrad Witz Nel Suo Capolavoro Di Ginevra

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Konrad Witz, tedesco di origine, ma attivo soprattutto in Svizzera fra il 1431 e il 1445 circa, è, per dirla con le parole dello storico dell'arte Jonathan Jones, "un gigante della pittura medievale che aspetta solo di essere scoperto". Le opere superstiti di questo artista sono davvero poche; fra queste sicuramente le più importanti sono le due tavole dipinte nel 1444 su entrambi i lati per l'altare maggiore della Cattedrale di Ginevra ed ora conservate nel Musée d'art et d'histoire de Genève[1]. Il presente studio illustra i risultati della campagna diagnostica condotta, prima dell'intervento di restauro, sui materiali costitutivi, la tecnica esecutiva e lo stato di conservazione di queste opere. Le indagini scientifiche sono state condotte dapprima mediante tecniche strumentali non invasive, successivamente su microcampioni prelevati in modo mirato dopo l'acquisizione dei dati delle analisi preliminari.
Gli obiettivi delle indagini sono così sintetizzati:

- osservazione in situ della superficie delle opere mediante l'impiego di microscopia a bassi ingrandimenti, in luce visibile e UV, per osservare lo stato di conservazione della pellicola pittorica originale e differenziare le parti originali dalle eventuali ridipinture;
- analisi XRF in più punti delle superfici policrome per avere dati preliminari sulla composizione degli elementi chimici e orientare la scelta dei prelievi di campione;
- esame chimico-stratigrafico di campioni di materiale pittorico per documentare la composizione delle stratificazioni dei materiali costitutivi, dalla preparazione fino alle vernici superficiali, e avere così informazioni circa la tecnica esecutiva;
- identificazione delle cariche minerali negli strati preparatori e dei pigmenti nelle stesure pittoriche;
- riconoscimento, mediante test microchimici ed istochimici, delle classi di appartenenza dei leganti organici nelle varie stratificazioni;
- identificazione dei leganti pittorici mediante gascromatografia abbinata alla spettrometria di massa (GC-MS).

Una prima ricognizione delle superfici pittoriche delle quattro opere è stata effettuata mediante l'impiego di uno stereo-microscopio operativo con sorgenti di luce visibile e UV. Successivamente, sono state analizzate le superfici pittoriche mediante uno spettrofotometro portatile a raggi X (XRF). Sui dipinti sono state, inoltre, eseguite indagini radiografiche e riflettografiche all'IR per studiarne lo stato di conservazione e esaminare i dettagliati disegni preparatori. Una volta acquisite in situ tutte queste informazioni sono stati effettuati sedici microprelievi di materiale pittorico in zone ritenute maggiormente significative in relazione alle domande di conoscenza.
I test microanalitici impiegati sono stati finalizzati alla ricerca di sostanze proteiche, composti saponificabili e polisaccaridi. Le analisi rivolte all'identificazione dei leganti organici sono state condotte mediante microspettroscopia infrarossa a trasformate di Fourier e gascromatografia accoppiata alla spettrometria di massa (GC/MS).

Reference
1. C. Lapaire, A. Rinuy; "Le retable de la cathédrale de Genève", in 'Zeitschrift für Schweizerische Archaologie und Kunstgescheichte', Band 44, 1987
.

Towards the Non-invasive Proteomic Analysis of Cultural Heritage and Archaeological Objects

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During the last years, there has been a growing interest in the identification of proteinaceous material of cultural heritage and archaeological objects. Our group recently developed a new method for the non-invasive analysis of proteins material from precious and ancient artworks. The technique uses a functionalized film that extracts the proteins from the surface of the object. The extracted proteins are then analyzed by LC-MS/MS analysis using shotgun proteomics[1].
In this research, we will present the application of this method to several historical and archaeological samples. Moreover, we will discuss the analytical performances for the identification and quantification of proteins in complex matrixes.
In particular, we will present the developed protocol and the results obtained from the analysis of several artworks: a polychrome wooden altarpiece from the Maestro of Oropa, a polychrome sandstone capital, a rare polychrome alabaster, several wood medieval and renaissance panels (Pietro Gallo from Alba, Defendente Ferrari, Martino Spanzotti, Jean Bapteur, Gerolamo Giovenone) and a detached fresco from Antoine de Lonhy.
Moreover, through the use of this method we were able to identify the animal origin of an old precious manuscript from Domenico della Rovere (XIV century) as well as the binders from a rare sample of painted leather casket from Parisian manufactory (beginning of XIV century).
The analysis of the bottom of several greek vessels (Pyxis, Krater, Kylix cup and Kantharos) revealed the presence of animal origin proteins.
In conclusion, this study will report the first use of this non-invasive method for the characterization of proteins from ancient objects without the need to transport or sampling the artifacts.

Reference
1. M. Manfredi, E. Barberis, F. Gosetti, E. Conte, G. Gatti, C. Mattu, E. Robotti, G. Zilberstein, I. Koman, S. Zilberstein, E. Marengo, P. G. Righetti; "Method for Noninvasive Analysis of Proteins and Small Molecules from Ancient Objects"; *Anal. Chem.*; 2017, *89*, 3310−3317.

Provenance of Bitumen from Different Apulian Bronze Age Settlements Through a Biomarker Based Approach

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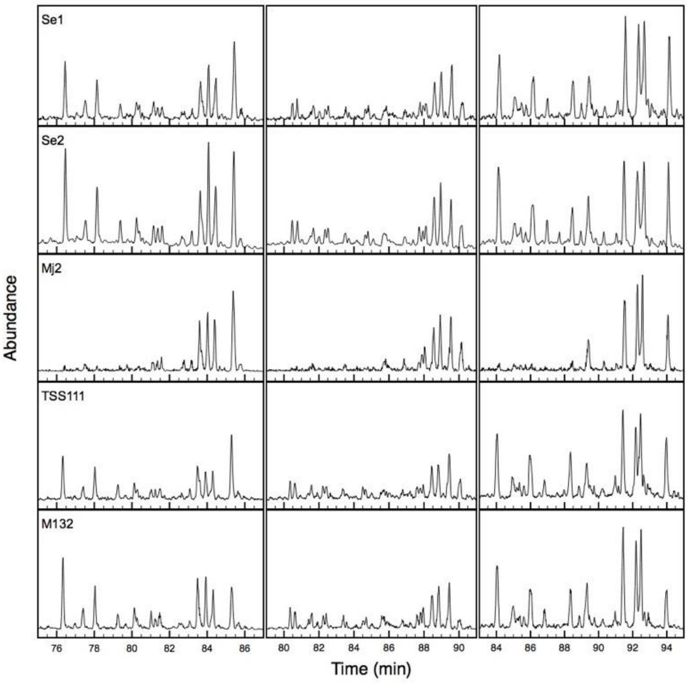
Bitumen has been used frequently in the Near East throughout history until modern times. Natural bitumen, found in solid or liquid form, was exploited and processed by ancient populations in Egypt, Mesopotamia and Syria for several uses such as to repair broken pottery, to waterproof containers or boats, to build the massive ziggurat temple mounds or to haft composite flint tools[1,2,3]. Together with the more widely studied and archaeologically important bitumen deposits in the Near East and Middle East[4,5], there are several seepages in Central Mediterranean which deserve more attention with respect to their exploitation and circulation in Antiquity. Evidence of bitumen use was found at several Apulian Bronze Age coastal sites[6], such as Otranto, Roca, Le Pazze (Lecce), Scoglio del Tonno (Taranto), Monopoli (Bari) and Torre Santa Sabina (Brindisi), but there are no archaeometric data about the relevant source(s).
Different bitumens from the central mediterranean sea region were studied as a possible source and analysed together with the archaeological samples using a geochemical, biomarker-based approach. The compositions of geological and archaeological samples were determined and provenance established. In the present communication, the relevant results will be described.



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References
1. Connan J., Nieuwenhuyse, O., Van As A., Jacobs L.; "Bitumen in early ceramic art: Bitumen-painted ceramics from Late Neolithic Tell Sabi Abyad (Syria)"; Archaeometry, 2004, *46*, 115-124.
2. Connan J.; "Le bitume dans l'Antiquité"; Éd. Errance, collection Les Héspérides, Arles, 2012.
3. Moorey P.R.S., 1999. Ancient Mesopotamian materials and industries: The archaeological evidence. Eisenbrauns, Winona Lake, Indiana.
4. Nissenbaum, A., Buckley, S., 2013. Dead sea asphalt in ancient Egyptian mummies—why? Archaeometry 55, 563-568.
5. Connan, J., Van de Velde, T., 2010. An overview of bitumen trade in the Near East from the Neolithic (c.8000 BC) to the early Islamic period. Arabian Archaeology and Epigraphy 21, 1-19.
6. Guglielmino, R., 2012. Il bitume di Roca. Breve nota su una sostanza negletta negli studi di protostoria italiana. Annali della Scuola Normale Superiore di Pisa 4/2, 99-114.

From XAES signals to depth-profile reconstruction: the case of copper and copper alloys

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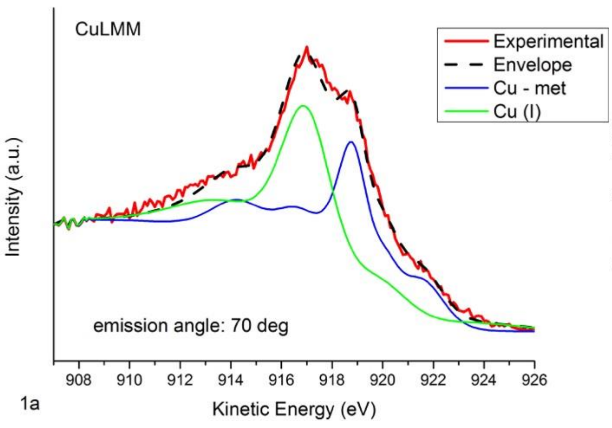
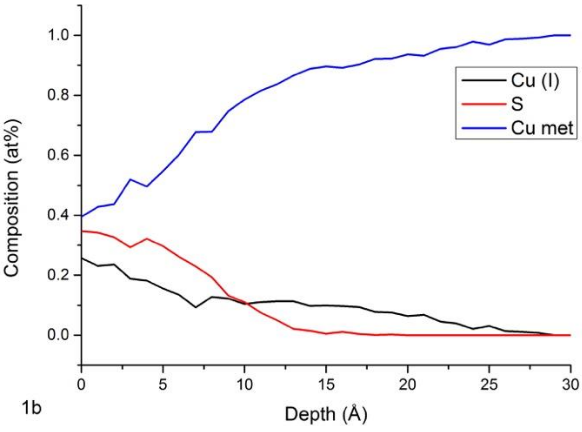
The analysis of the chemical state of co-existing copper and Cu (I) compounds by XPS is difficult since the Cu2p signal does not show any chemical shift. On the contrary the XAES signal $CuL_3M_{45}M_{45}$ allows distinguishing between Cu (0) and Cu (I) compounds. An analytical method starting from curve fitting of composed Auger induced CuLMM signals based on standards that permits quantifying the amount of copper and Cu_2O on the surface of brasses was developed and the thickness of the contamination and oxide nanolayers on the brass samples was determined by applying the three-layer model to standard XPS signals[1]. An alternative non-destructive way to reconstruct the in-depth composition profile of a nano-layered surface by XPS involves the acquisition of angle resolved XPS spectra. An ARXPS experiment provides information on the intensities of the photoelectron signals vs emission angle: the higher is the emission angle, the more intense are the signals of the elements in the most external layer. To transform this ARXPS information in concentration vs depth, an iterative protocol based on the maximum entropy method (MEM)[2] can be applied. In this work the depth profile of a S-functionalized copper sample, before and after rubbing in a tribometer was reconstructed applying MEM. The functionalization of copper with sulfur lead to the formation of Cu(I) – S bonds. The curve fitting of CuLMM (Figure 1a) allowed quantifying the % of Cu2p due to metallic copper and to Cu (I) in order to obtain the apparent concentration graph, which is the input for the MEM routine. The in-depth distribution obtained is shown in Figure 1b.





Results obtained also on the in-depth reconstruction of the oxide layer on the surface of brass alloys aged in buffer phosphate solution at pH 7 will be presented and discussed.

References
1. F. Cocco, B. Elsener, M. Fantauzzi, D. Atzei, A. Rossi; "Nanosized surface films on brass alloys by XPS and XAES"; *RSC Advances*, 2015, *6*, 31277-31289.
2. M. A. Scorciapino, G. Navarra, B. Elsener, A. Rossi; "Nondestructive Surface Depth Profiles from Angle-Resolved X-ray Photoelectron Spectroscopy Data Using the Maximum Entropy Method"; I. A New Protocol; *J. Phys. Chem. C*, 2009, *113*, 21328–21337.

Integrated Approach for the Chemical Characterization of Archaeological Woods

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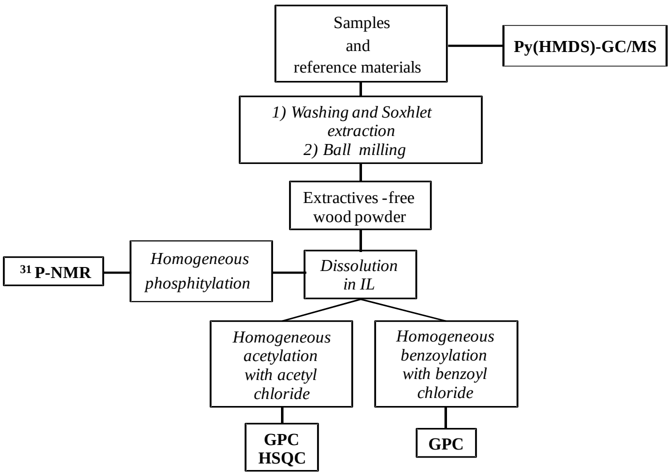
Wet archaeological wooden artefacts represent a conservation challenge still far to be solved, especially when archaeological wet wood has been previously treated with unstable materials and/or contain unstable inorganic salts which influence the degradation pathways. In order to evaluate the state of conservation of archaeological wet wood we have developed since 2007 an integrated analytical approach based on NMR spectroscopy, Py-GC/MS, and GPC analysis and applied on woods from the Site of the Ancient Ships of San Rossore[1,2,3](Pisa, Italy) and Vasa[4]. Recently we have improved the analytical approach by dissolving archaeological wood into ionic liquids (ILs) as non-derivatizing solvents: in fact, 1-allyl-3-methylimidazolium chloride ([amim]Cl) can provide a homogeneous reaction medium for derivatization of wood-based lignocellulosic materials. As a result, the functionalised wood developed an enhanced solubility in molecular solvents, thus enabling information about modifications of lignin, depolymerisation of cellulose and structure of lignin-carbohydrate complexes to be obtained by means of spectroscopic (2D-HSQC-NMR and ^{31}P-NMR) and chromatographic (Gel Permeation Chromatography) techniques. Py-GC-MS was used to investigate the degradation undergone by the lignocellulosic components on the basis of their pyrolysis products, without any pre-treatment of the samples [Figure 1]. The application of all these combined techniques provided a comprehensive characterisation of the whole cell wall of archaeological wood and the evaluation of its state of preservation. These analytical techniques were applied in an integrated way for the first time on archaeological wood from the Oseberg collection. High depletion of carbohydrates and high extent of lignin oxidation were highlighted in the alum-treated objects, whereas a good preservation state was found for the untreated wood of the Oseberg ship (Norway)[5].



References
1. Colombini M.P., Orlandi M., Modugno F., Tolppa E.-L., Sardelli M., Zoia L.; "Archaeological wood characterisation by PY/GC/MS, GC/MS, NMR and GPC techniques"; *Microchem. J.*, 2007, *85*(1), 164-73.
2. Colombini M.P., Łucejko J.J., Modugno F., Orlandi M., Tolppa E.-L., Zoia L.; "A multi-analytical study of degradation of lignin in archaeological waterlogged wood"; *Talanta*, 2009, *80*, 61-70.
3. Salanti A., Zoia L., Tolppa E.L., Giachi G., Orlandi M.; "Characterization of waterlogged wood by NMR and GPC techniques"; *Microchem. J.*, 2010, *95*, (2), 345-52.
4. Zoia L., Salanti A., Orlandi M.; "Chemical characterization of archaeological wood: Softwood Vasa and hardwood Riksapplet case studies"; *Journal of Cultural Heritage*, 2015, *16*(4), 428-437.
5. L. Zoia, D. Tamburini, M. Orlandi, J.J. Łucejko, A. Salanti, E.-L. Tolppa, F. Modugno, M. P. Colombini; "Chemical Characterisation of the Whole Plant Cell Wall of Archaeological Wood: An Integrated Approach"; *Analytical and Bioanalytical Chemistry*, 2017, doi:10.1007/s00216-017-0378-7.

Rapid, Low-cost and Portable Electrochemical Assay for Heart Injury Diagnosis

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Early and fast diagnosis and prognosis of heart injury are of paramount importance for a successful treatment of the diseases. Furthermore, heart related pathologies, also caused by anticancer treatment, are determinant in cancer patient survival. Several molecular markers of heart damage are emerging and electrochemically-driven trapping and signal transduction of biomarkers have proven to be effectively employed in the development of sensing devices and assays.

For instance, cytochrome c (cyt c), an inner mitochondrial membrane (IMM) protein, which plays an important role in oxidative phosphorylation, can be detected as heart failure marker. This protein is not detectable in healthy patients' blood but it has been demonstrated that during some diseases, which also involves the cellular apoptosis, cyt c is released[1]. In particular, cyt c is released from cellular membrane as a consequence of the treatment of infarction[2]. A fast monitoring of cyt c concentration can help to control the progression and extension of the heart injury guiding the therapeutic actions.

In this view, there is an urgent need to develop biochips/sensors/devices for the rapid detection of markers, such as cyt c, in very early stages of the diseases to evaluate the real state of the injury and to operate with fast bedside therapies.

Herein, we show some strategies based on optimized chemical affinity for the trapping and the detection of heart injury markers and for signal amplification.

References
1. V.E. Kagan et *al.*; *Free Radical Biol. Med.*, 2009, *46*, 1439-1453.
2. G. Marenzi et *al.*; *Am. J. Cardiol.*, 2010, *106*, 1443-1449.

Carbon Black Modified Screen-Printed Electrodes to Detect Chlorine Dioxide

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Chlorine compounds have always been the most used chemical agents for water disinfection. However, alternative disinfectants have been investigated to avoid harmful by-products generated by the reaction between free chlorine and organic substances present in water. Among the different compounds used for the treatment of water, chlorine dioxide can be considered a good alternative to chlorine. Chlorine dioxide is employed in several industrial fields, including food, textile, and paper industries. Furthermore, chlorine dioxide is used to produce disinfected water with satisfactory characteristics in terms of odor and taste[1,2].

Chlorine dioxide is often used because of its excellent oxidizing and disinfecting properties against bacteria, viruses and algae, combined with the absence of harmful by-products, such as trialomethanes. Moreover, it is active in a wide range of pH, unlike free chlorine[3].

Actually, the maximum residual disinfectant level using chlorine dioxide in water is 0.8 ppm, accordingly to the United States Environmental Protection Agency (EPA), thus analytical tools are required to control the disinfectant level[4].

Due to the industrial needs in the control of disinfectant level in different processes, the development of cost-effective and easy to use sensors is highly requested.

The goal of the Tecnosens Spin-off is to fabricate miniaturized and sustainable electrochemical sensors for the monitoring of disinfectant compounds.

Herein, we report a novel and cost-effective probe for the *in-situ* determination of chlorine dioxide in swimming pool water.

This sensor was fabricated using screen-printed electrodes modified with carbon black (CB), a cost effective and raw nanomaterial with excellent electrocatalytic properties as demonstrated by our research group and corroborated by also other groups, like Compton's group[5,6].

The working electrode was modified by drop casting with 2 µl of a carbon black dispersion (1 mg/ml) prepared in a mixture of N,N-Dimethylformamide/H_2O 1:1 (v/v). Under optimized conditions (potential of + 0.1 V vs Ag/AgCl and Britton-Robinson buffer 0.02 M + KCl 0.02 M, pH =2 as working solution), the sensor showed a linear response up to 10 ppm (R=0.989), sensitivity and LOD equal to 13.4 nA/ppm and 0.03 ppm, respectively.

The interfering species including NO_3^-, SO_4^{2-}, CO_3^{2-}, HCO_3^- and Cl^- were evaluated, demonstrating the selectivity of this device.

The study of matrix effect and the accuracy of the sensor was estimated in swimming pool water, obtaining a satisfactory recovery value (78 ± 8)%.

References

1. Edition, Fourth. "Guidelines for drinking-water quality." WHO (2011).
2. Aieta, E. Marco, and James D. Berg; "A review of chlorine dioxide in drinking water treatment"; *Journal (American Water Works Association)*, 1986, 62-72.
3. Gagnon G. A., et *al*.; "Disinfectant efficacy of chlorite and chlorine dioxide in drinking water biofilms"; *Water Research*, 2005, 39.9, 1809-1817.
4. "Il biossido di cloro." Caffaro Brescia S.p.A, 2014.
5. Arduini Fabiana et *al.;* "Carbon Black-Modified Screen-Printed Electrodes as Electroanalytical Tools"; *Electroanalysis*, 2012, 24.4, 743-751.
6. Lo, Tsz WB, Leigh Aldous, and Richard G. Compton; "The use of nano-carbon as an alternative to multi-walled carbon nanotubes in modified electrodes for adsorptive stripping voltammetry"; *Sensors and Actuators B: Chemical,* 2012, 162.1, 361-368.

Bacillus Anthracis Spores Detection By Using A Label Free Impedimetric Aptasensor

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Since 1930, biological weapons have been developed and used in different countries; they include microorganisms like virus and bacteria which can be used in terroristic attacks, affecting the human health. For instance, *Salmonella typhimurium* was spread in food samples by a religious sect in the western USA; *Bacillus anthracis* spores were used in 2001 to contaminate letters in the Washington area[1].

For the safety of citizens at worldwide level, there has been a continuous interest in the development of robust and reliable analytical tools for the detection of these agents, to provide an early alarm in case of terroristic attacks. The detection of these agents is usually carried out using laboratory-set techniques like real-time PCR, which are not suitable for in field applications and fast early warning, due to the lack of portability, power requirements, long response time and expensive procedures. In this context, electrochemical biosensors offer advantages in terms of high sensitivity, miniaturization, integration, low cost, and power requirements. For the development of biosensors able to detect these agents, antibodies are mainly used as biocomponents, but their production requires the use of animals; in addition, their stability is often affected by environmental conditions. To overcome these drawbacks, synthetic DNA aptamer sequences were recently employed to develop aptasensors[2].

Herein we describe the development of an impedimetric label free biosensor for the detection of *B. anthracis* spores, using the BAS-6R aptamer as biocomponent. This aptamer sequence has been selected among a library of 92 DNA aptamers by Bruno et al., demonstrating a good selectivity for *Bacillus* spores when tested in fluorescence, using a fluorophore and a quencher as labels[3]. We developed a miniaturized label free aptasensor for *B. anthracis* spores using this aptamer as biocomponent and the electrochemical impedance spectroscopy as technique. The aptamer BAS-6R was immobilised on gold screen-printed electrodes by exploiting the affinity between the gold working electrode area and the thiol chain at the 5′ position of BAS-6R, while the spores presence has been detected by evaluating the increase of the charge transfer resistance (R_{ct}). To optimise the aptasensor, different working conditions, including the amount of aptamer and blocking agent, the time of aptamer incubation, the type of working buffer have been studied. This aptasensor was then tested against *B. anthracis* spore simulants, namely *Bacillus Cereus 14579*, *Bacillus Subtilis*, *Bacillus Cereus* 11778, observing a significant R_{ct} variation in the presence of *B. Cereus 14579* (10^5 CFU/mL), thus demonstrating the binding between the aptamer and this *Bacillus*. This aptasensor has showed the capability to detect *B. anthracis* spores simulant in the range comprised between 0.5×10^5 CFU/mL and 7×10^5 CFU/mL, it has also demonstrated its suitability for a rapid analysis.

References

1. Roffey, R., Lantorp, K., Tegnell, A., & Elgh, F.; *Clinical microbiology and infection*, 8, 522-528.
2. M. Labib, A.S. Zamay, O.S. Kolovskaya, I.T. Reshetneva, G.S. Zamay, R. J. Kibbee, S.A. Sattar, T. N. Zamay, M.V. Berezovski; *Anal. Chem.*, 84, 8966−8969.
3. J.G. Bruno, M.P. Carrillo; *J. Fluoresc.*, 22, 915–924.

A Reagent-Free Paper-Based Biosensor For The Detection Of Mustard Agents

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Mustard Agents (MAs) are among the most dangerous Chemical Weapon Agents (CWAs) used during the last wars because they cause severe toxic effects on living organisms as typical skin lesions similar to burns. They embrace sulphur mustards, such as Yperite (bis(2-chloroethyl)sulphide), and nitrogen mustards, such as HN1 (bis(2-chloroethyl)ethylamine), HN2 or Mustine (bis(2-chloroethyl)methylamine), and organic arsenical Lewisite (dichloro(2-chlorovinyl)-arsine). Such kind of CWAs still represent a potential threat within the current international scenario, because of the concrete possibility that they could be used for terrorist attacks. Indeed, the Organization for the Prohibition of Chemical Weapons (OPCW) has accused Isis to have used MAs in Syria and Iraq, while ONU discovered a CWA factory nearby the city of Ninive, with several cases of people contaminated by MAs after the battle to liberate Mosul.

Classical analytical techniques such as Gas Chromatography and Liquid Chromatography are usually used for the analysis of these compounds. Electrochemical sensors represent an interesting alternative, since they can be tailor-made to improve the sensitivity and the selectivity. As they can be associated with portable, easy-to-use, and cost-effective instrumentation, they could result in user-friendly and fast alarm devices particularly suitable in case of chemical attack as well as screening tools for contaminated areas.

Recently, we have developed an amperometric bioassay for MAs detection by means of a polyester-based screen-printed electrode (SPE) modified with Prussian Blue nanoparticles[1]. Herein, we present the preliminary results obtained for MAs detection by using a filter paper-SPE, printed with a graphite-based ink containing a hybrid nanocomposite of Carbon Black and Prussian Blue nanoparticles (CBPBNPs). The use of paper as a support, further reduces the cost of the sensor, facilitates its disposal and paves the way for the construction and assembling of a reagent-free sensor. MAs simulant bis(2-chloroethyl)amine was detected by exploiting its inhibition activity toward the choline oxidase enzyme (ChOx). Choline (Ch) was used as a substrate to monitor the enzymatic activity, through the measurement of the by-product hydrogen peroxide at an applied potential of 0 mV vs Ag/AgCl. Hence, the analytical performances of CBPBNPs-based paper-SPE for hydrogen peroxide detection were investigated. The known properties of CBPBNPs to electrocatalyse the hydrogen peroxide reduction[2] allowed to enhance the analytical performances of the paper-SPE, obtaining a linear range between 0.1 and 10 mM, with a sensitivity of 3.03 $\mu AmM^{-1}cm^{-2}$. Then, the enzymatic activity of choline oxidase toward choline was studied in the range of 0.1 and 20 mM, obtaining an apparent K_M of 6.1±0.5 mM. The inhibition of ChOx was thus observed by using bis(2-chloroethyl)amine from 1 to 25 mM, resulting in a linear range up to 7.5 mM, with IC_{50} = 5.4 mM and a LOD equal to 0.4 mM. Furthermore, the possibility to realize a reagent-free detection system was explored by loading Ch and ChOx on an origami-inspired sensor, in order to obtain a ready-to-use amperometric device for the fast and selective analysis of MAs.

References
1. F. Arduini, et *al.*; *Sensors*, 2015, *15*, 4353-4367.
2. S. Cinti, et *al.*; *Electrochemestry Communications*, 2014, *47*, 63–66.

Development Of A Suitable Sequential Extraction Procedure For The Assessment Of The Availability And Reactivity Of Metal Species In Arctic PM_{10} Samples

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Most of the studies on the atmospheric particulate matter (PM) trace metal content consist of the determination of the total concentrations, without distinguishing between the various chemical forms of each element. This procedure does not give any information on the different sources of PM and often provides an overestimate of potential metal toxicity, as only the soluble fraction is likely to interact with the environment and living beings. Unfortunately, the chemical complexity of PM, the extremely small particle sizes and the small quantity of sample typically collected can pose significant problems for metal speciation. In many cases the exact distribution of an element among well-defined chemical species is impossible to determine, due to the large numbers of individual species and to the lack of a universal analytical technique able to both identify and quantify all of them. Alternatively, fractionation procedures are often applied, and the classification of analytes is made according to physical (e.g., size, solubility) or chemical (e.g., bonding, reactivity) properties. This kind of classification is a valid instrument for both the identification of emission sources[1] and the evaluation of health and environmental impact[2].

Many researchers have worked on the design of extraction schemes for the sequential solubilization of metals from sediments, leading to the development of the commonly accepted three-steps BCR protocol. The adaptation of this extracting scheme to PM samples led to the development of two-steps procedures, considered a good compromise among costs, analytical times and achievable information. However, different extracting solutions, different extraction methods (ultrasounds, microwave, stirring, prolonged contact) and different techniques for the separation of the extract from the solid residue (filtration, centrifugation) are used, thus reducing the possibility to compare the results[3].

In this study the most common extracting solutions for PM fractionation have been compared: i) deionized water, due to its high representativeness of the natural solubility processes taking place in the environment; ii) diluted acetic acid, also reported in the BCR fractionation protocol, allowing a good control of the external factors that could influence the extraction and iii) a buffer solution, (ammonium acetate buffer, pH 4.5), able to maintain a good pH control throughout the extraction; the selected pH is very similar to the PM spontaneous one, in order to mime the interactions naturally occurring in the environment[4]. A two-step sequential extraction scheme was optimized by using three Certificate Reference Materials (BCR176 "City waste incineration ash", NIST1648a "Urban particulate matter" and BCR701 "Lake sediment") and comparing the results obtained applying different extraction methods and different extracting solutions. The optimized procedure was then applied to some Arctic PM_{10} samples.

References
1. Canepari S., Pietrodangelo A., Perrino C., Astolfi M.L. and Marzo M.L., *Atmos Environ*, 2009, 43 (31), 4754-4765.
2. Pelfrêne A., Cave M.R., Wragg J. and Douay F., *Int J Env Res Pub He*, 2017, 14 (112), 1-15.
3. Dabek-Zlotorzynska E., Kelly M., Chena H. and Chakrabarti C.L., *Anal Chim Acta*, 2003, 498 (1-2), 175-187.
4. Canepari S., Astolfi M.L., Moretti S. and Curini R., *Talanta*, 2010, 82 (2), 834-44.

DNA-based single step fluorescence detection of Domoic Acid in marine water

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Domoic Acid is a neurotoxin produced by various species of red microalgae and diatoms during the harmful algal bloom. This potent toxin affects human health through the consumption of contaminated shellfish and finfish or through water or aerosol exposure. Therefore, early detection of algal toxins is an important aspect for public safety and natural environment[1,2].

Here we have developed the first homogeneous competitive fluorescence DNA-based assay for the detection of Domoic Acid. Specifically, this assay is based on the competition between Domoic Acid conjugated with two different DNA strands and free Domoic Acid for the binding of anti-Domoic Acid antibodies. By employing this strategy, we are able to achieve single-step, label free detection of Domoic Acid in marine water without sample pre-treatment at very satisfactory level of concentrations.

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References
1. F.M. Van Dolah; *Environmental Health Perspectives*, 2000, *108*, 133-141.
2. A.F. Saeeda, S.A. Awanb, S. Linga, R. Wanga, S. Wanga; *Algal Research*, 2017, *24*, 97-110.

Development of an analytical strategy for the purification and identification of bioactive peptides from microalgae

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Food components have demonstrated biological activities that are being applied in the prevention, management and treatment of health conditions, including cardiovascular disease. The use of food protein-derived bioactive peptides as functional ingredients in foods is a rapidly developing area of food innovation. Bioactive peptides are short-chain proteinogenic amino acid residues joined by peptide bonds, and are produced by enzymatic cleavage of proteins during food digestion, microbial fermentation, food processing, or exogenous enzymatic hydrolysis. The interest in the functional food application of peptides is due to their demonstrated biological activities relevant to the management of human health conditions such as hypertension, oxidative stress, cancer, diabetes, inflammation, and immune disorders. Therefore, there is a need to identify sustainable protein sources and optimize technology for their isolation for niche applications. One area of current focus is the valorization of protein-rich secondary products of the agri-food industry, especially dairy whey, oilseed and fish processing meals. Moreover, marine microalgae have been identified as attractive and sustainable protein sources for industry-scale production of bioactive peptides[1]. Generally, microalgae contain 40-70% proteins, 12-30% carbohydrates, 4-20% lipids, 8-14% carotene and substantial amounts of vitamins B1, B2, B3, B6, B12, E, K, and D [2]. Importantly, microalgae proteins contain well-balanced amino acid profiles, comparable to those of egg, soybean and the FAO/WHO [3] reference pattern; however, microalgae proteins may have lower biological values, digestibility, net protein utilization and protein efficiency ratio than the gold standard, casein, and egg[2]. Microalgae synthesize all 20 proteinogenic amino acids and can be unconventional sources of essential amino acids for human nutrition. Nowadays, there are numerous commercial applications of microalgae. For example, (i) microalgae can be used to enhance the nutritional value of food and animal feed owing to their chemical composition, (ii) they play a crucial role in aquaculture and (iii) they can be incorporated into cosmetics[4].

The aim of this study was the development of an analytical strategy for the production of purified bioactive peptides from microalgae proteins, by testing 7 different extraction protocols and screening different enzymes for protein hydrolysis. The purification of peptides was carried out by multidimensional liquid chromatography. The resulting fractions were tested for antihypertensive and antioxidative activities. The most active ones were characterized by nano-liquid chromatography-tandem mass spectrometry and identified by database search. The identified peptides were further mined by in-silico analysis using PeptideRanker to ascribe a bioactivity rank to each peptide. Thus, potential bioactive peptides were synthesized and validated checking their retention times and fragmentation patterns for consistency.

References
1. C.E.C.C. Ejike, S. A. Collins, N. Balasuriya, A. K. Swanson, B. Mason, C. C. Udenigwe; "Prospects of microalgae proteins in producing peptide-based functional foods for promoting cardiovascular health"; *Trends in Food Science & Technology*, 2017, *59*, 30–36.
2. E.W. Becker, Micro-algae as a source of protein Biotechnology Advances, (2007) 25, 207–210.
3. FAO/WHO (Food and Agricultural Organization of the United Nations/World Health Organization); "Energy and protein requirement"; Report of a Joint FAO/WHO ad hoc Expert Committee, FAO, 1973, 52.
4. P. Spolaore, C. Joannis-Cassan, E. Duran, A. Isambert; "Commercial applications of microalgae"; *Journal of Bioscience and Bioengineering*, 2006, *101*, 87–96.

Investigation of mass transfer phenomena in new core-shell and sub-2µm fully porous chiral stationary phases for ultrafast high-performance enantioseparations

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During the last decade, the field of chiral separations experienced a radical transformation. The attention of scientists and manufacturers shifted from the research of novel chiral stationary phases (CSPs) characterized by enhanced enantioselectivity to the preparation of new CSPs suitable for high-efficient ultrafast (less than 1 minute) enantioseparations. To this purpose, kinetically high efficient particle formats, such as sub-2µm fully porous particles (FPPs) and superficially porous ones (SPPs), have been introduced in chiral chromatography and functionalized with already known chiral selectors. However, the transition from traditional enantioseparations (usually performed on 3-5 µm FPPs) to ultrafast ones has been slowed down by the lack of complete understanding of the complex mass transfer phenomena in chiral chromatography and by the practical difficulties in functionalizing small particles with chiral selectors.[1]

In this work, a Pirkle-type chiral selector (Whelk-O1) was used to functionalize both SPPs and FPPs of different diameter (including also sub-2µm fully porous ones). The CSPs were slurry packed at high pressure into columns of different geometries. The kinetic performance of these columns was evaluated in normal phase conditions for the separation of the two *trans*-stilbene oxide (TSO) enantiomers[2].

The results of peak parking experiments were interpreted in the light of a proper model of diffusion in porous media (the so-called time-averaged or parallel model was used)[3] and each contribution to band broadening was individually determined. The results shown that eddy dispersion and adsorption-desorption kinetics are the most important contributions that control the efficiency of these columns. Additionally, to further assess the potential of these new CSPs for ultrafast enantioseparations, short columns (10 mm long) were packed with both sub-2µm and core-shell Whelk-O1 CSPs and operated at a very high flow rate (8 mL/min) to perform the separation of TSO enantiomers in less than one second[2].

References
1. M. Catani, O. H. Ismail, F. Gasparrini, M. Antonelli, L. Pasti, N. Marchetti, S. Felletti and A. Cavazzini; *Analyst*, 2017, *142*, 555-566.
2. O. H. Ismail, L. Pasti, A. Ciogli, C. Villani, J. Kocergin, S. Anderson, F. Gasparrini, A. Cavazzini and M. Catani; *J. Chromatogr. A*, 2016, *1466*, 96-104.
3. J. H. Knox and H. P. Scott; *J. Chromatogr.*, 1983, *282*, 297–313.

Integration of separation-based analytical platforms in the development of nanomaterials as bioactive products

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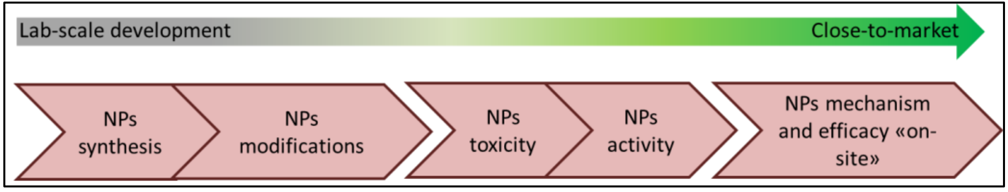
Silver nanoparticles are a promising tool to control bacterial infections, and their production and optimization is an expanding field. However, the controlled production of particles with specific properties clashes with the lack of suitable techniques to provide characterization of the newly-produced materials. This research focused on the development of a suitable analytical platform able to achieve a multiparametric assessment of nanoparticle suspensions, and its integration in the development of bioactive nanoproducts in a safety-by-design approach.



The analytical platform designed was applied in the various steps of nanoparticles synthesis and application, to provide reliable information and correlate nanoparticles properties and effects.

The separation technique used for this task was Hollow-fiber flow field-flow fractionation (HF5) coupled with UV, Multi angle light scattering (MALS) and atomic absorption detectors. The particles are characterized, separated from the unreacted media and the ionic fraction, collected and stored. Different silver nanoparticles have been tested to correlate the particles antiseptic activity and toxicity to their physicochemical properties, differing for coating and ionic content. These preparations were characterized in terms of size, shape, charge and free Ag+ amount [1].

Safety aspects were addressed by studying toxicity, inflammatory response and cellular recovery upon exposure of skin models to Ag NPs. The real time effects of the AgNPs on bacteria were also evaluated. The results obtained show that nanoparticles' activity depends not only on ionic/nano Ag ratio but also on size and surface charge of the particle[2]. An interesting effect of the positively coated Ag NPs has been observed even though the ionic/nano silver ratio is the lowest amongst all the materials tested. More importantly, these particles –though weakly toxic for human skin- remained active for greater than 7 days and remained micro-biocidal on re-challenge with freshly inoculated bacterial. By rationalizing the property-effect relationships between the evaluated parameters it was possible to categorize the key properties needed to predict nanoparticle activity, and extrapolate which combination of physicochemical properties is recommended for a successful antiseptic medical device.Then, to investigate the "nano" related risk and toxicity mechanism of silver nanoparticles and to extend this study to their close-to-market application, optimized nanoparticles were tested for NP release upon wetting/wear off. The samples collected were compared with FFF-isolated AgNPs: This approach proved to be effective and able to distinguish amongst candidates, providing a useful tool for the fast screening of nano-sized coating agents.

References
1. Marassi, V.; Roda, B.; Casolari, S.; Ortelli, S.; Blosi, M.; Zattoni, A.; Costa, A. L.; Reschiglian, P., Hollow-fiber flow field-flow fractionation and multi-angle light scattering as a new analytical solution for quality control in pharmaceutical nanotechnology. *Microchemical Journal*.
2. Ivask, A.; Elbadawy, A.; Kaweeteerawat, C.; Boren, D.; Fischer, H.; Ji, Z.; Chang, C. H.; Liu, R.; Tolaymat, T.; Telesca, D.; Zink, J. I.; Cohen, Y.; Holden, P. A.; Godwin, H. A., Toxicity mechanisms in Escherichia coli vary for silver nanoparticles and differ from ionic silver. *ACS Nano* 2014.

Coumarin-3-carboxylic acid as ligand: acid–base properties, interactions with Fe^{3+} and characterization of complexes in aqueous solution

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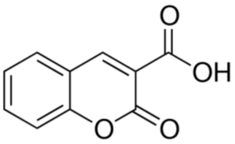
The aim of this work was to determine the sequestering ability of cumarin-3-carboxylic acid (Scheme 1, generally HCCA) towards iron (III) under the physiological conditions (*i.e.* 37° C and 0.16 M NaCl).



Scheme 1: Structure of HCCA.

The choice of the metal was related to the role that it plays in the biological systems and to its significant concentration in the body. Coumarins represent a new class of natural medicines potentially useful for the treatment of many diseases[1-6]. Many studies have been shown that the binding of a drug to a metal cation increases its activity, and the complex possesses much more therapeutical properties than parent drug.

The thermodynamic approach provides, first of all, the determination of the solubility and of the acidic constants of ligand under the selected experimental conditions. Then the formation constants of metal/ligand complexes were determined evaluating the competition between the protons and the iron towards ligand. The study was conducted by measuring with a glass electrode the free hydrogenation concentration in solutions containing different metal and ligand concentrations and different metal/ligand ratios, in order to determine the complexes and the corresponding stability constants $\beta_{p,q,r}$.

The investigated equilibrium can be expressed according to the following general equation:

$$p\ Fe^{3+} + r\ HCCA \rightleftarrows Fe_p(H)_{-q}(HCCA)_r^{(3p-q)+} + q\ H^+ \qquad \log \beta_{p,q,r} \pm 3\sigma$$

The characterization of the complexes was carried out with the aid of UV-Vis spectroscopy and by ICP-MS analysis.

References

1. R.J. Lewis, O.M.P. Singh, C.V. Smith, T. Skarzynski, A. Maxwell, A.J. Wonacott, D.B. Wingley, *Embo. J.*, **1996**, *15*, 1412.
2. W. Shilling, R. Longland, C. Crampton, *Nature*, 1969, *221*, 664.
3. Y.L. Chen, T.C. Wang, K.H. Lee, Y.L. Chang, C.M. Teng, C.C. Tzeng, *Helv. Chim. Acta*, 1996, *79*, 651.
4. C.M. Kam, J.E. Kerrigan, R.R. Plaskon, E.J. Daffy, P. Lollar, F.L. Suddath, J.C. Powers, *J. Med. Chem.*, 1994, *37*, 1298.
5. S. Manfredini, P.G. Baraldi, R. Bazzanini, M. Guarneri, D. Simoni, J. Balzarini, E.D. Clercq, *J. Med. Chem.*, 1994, *37*, 2401.
6. L. Pochet, C. Doucet, M. Schynts, N. Thierry, N. Boggeto, B. Pirotte, K.Y. Liang, B. Masereel, P. de Tulio, J. Delarge, M. Reboud-Ravaux, *J. Med. Chem.*, 1996, *39*, 2579.

Ion pair formation between tertiary aliphatic amines and perchlorate in the biphasic H_2O / CH_2Cl_2 system

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The ability of selected alyphatic amines, namely tripropylamine (TPrA), trisobutylamine (TisoBuA), and tributylamine (TBuA), to form ion pairs with perchlorate anion in biphasic aqueous/dichloromethane mixtures has been demonstrated by GC with flame ionization and mass detectors, and by NMR measurements. Aliphatic amines are not present in the organic phase when the aqueous solution is at acidic pH and no perchlorate is added, whereas they are transferred with high efficiency to the dichloromethane phase when the aqueous solution is added with perchlorate 0.1 M. The extraction efficiency was modeled by theoretical equations, obtained from the mass balances and mass action laws, which were used to fit the experimental GC data. The fitting procedures allowed to determine values for K_P (partition constant of the free alyphatic amines), K^{IP} (formation constant of the ion pairs), and K_P^{IP} (partition constant of the ion pair), for TPrA, TisoBuA, TBuA at 25 °C. NMR spectra in dichloromethane before and after partition showed the presence of R_3NH^+ in the organic phase after partition, and no evidences of such species before partition. Ion pairs were shown to form in dichloromethane also when perchlorate anion is replaced by other common monocharged inorganic anions such as nitrate, chloride, chlorate, dihydrogenophosphate, and iodate. The extracted fraction of the ion pair by these ions was however lower than that observed for perchlorate. No ion pairs formed when dichloromethane is replaced by n-hexane, suggesting that aliphatic amine ion pairs can form in polar organic solvents but not in non-polar ones. The ion pair formation affects the distribution of aliphatic amines between organic and aqueous phase, and it must therefore be considered when partition coefficients and solubility data are computed for these compounds in biphasic aqueous/organic mixtures.

Acid-base and chelating properties of Gantrez copolymers

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The Gantrez (GTZ) copolymers (GTZ AN169, GTZ S97 and GTZS95) are poly(methyl vinyl ether co-maleic acid) at high molecular weight (2000, 1200 and 220 kDa), in anhydride (AN) and acid (S) form, with important characteristics (high chelating power, excellent dispersion and antisoil redeposition properties) that allow to employ them in several applications: in cosmetic, medical and industrial products. The GTZs can be considered to be a good model molecule for the study of more complex natural macromolecules, such as natural organic matter, owing to rich in carboxylic groups, which acts as a binding site for organic and inorganic cations over a wide pH range. The GTZs, when dissolved in water, form sticky and jelly solutions due to the formation of micelles in solution. The determination of the critical micelle concentration (CMC) was determined by different techniques: light scattering, conductivity, surface tension and DOSY NMR [1]. The acid-base behavior of the GTZs were studied take into account the CMC, in widely range of temperature, ionic strength and different ionic media. In the calculation of the protonation constants, a simplified approach, the diprotic-like model, was used; the model allows to treat, from acid−base and complexing points of view, a polyelectrolyte like a simple low molecular weight ligand, considering a minimum number of protonation sites necessary to extensively depict the system and in the case of the GTZs, two methyl vinyl ether co-maleic units were considered.
From the analysis of the experimental data of GTZ AN169, S97 and S95, in the same experimental conditions of temperature, ionic strength and ionic medium, it was possible to observe a trend in the protonation constants, namely an increase of the basicity of the ligands, increasing the molecular weight. The binding ability of the three copolymers was studied towards two different metal cations, Zn^{2+} and Sn^{2+} in NaCl aqueous solutions at $I = 0.15$ mol dm^{-3} and $T = 298.15$ K. The speciation model of the GTZs were compared from them and sequestering ability of these polyelectrolytes was evaluated by means the empirical parameter pL_{50}.

References
1. Reference n. 1: C. Bretti, R. M. Cigala, F. Crea, C. De Stefano, G. Gattuso, A. Irto, G. Lando, D. Milea, S. Sammartano, *J. Chem. Eng. Data*, DOI: 10.1021/acs.jced.7b00101.

Coordination of a bis–histidine oligopeptide with Ga^{3+} ion in aqueous solution

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The development of radioisotopes of inorganic elements (as ^{68}Ga(III) and ^{188}Re(I)) has gained much interest in recent years for diagnostic and therapeutic application in nuclear medicine[1]. Small peptides are employed for complexing the radiometal in a biologically stable environment. They have some advantages: easy of synthesis and modification, tumor–penetrating ability and good biocompatibility[2].

Aim of the present work has been the interaction between Ga^{3+} ion with a bis–histidine oligopeptide, PHIS (Fig.1) in aqueous solutions, by the following methods: Potentiometry, Spectrofluorimetry, FT−IR and ^{1}H–NMR Spectroscopy as also by Circular Dichroism. All the measurements have been investigated at 25 °C in 0.1 M $NaClO_4$ media. Information on coordination sites are obtained with model molecule such as histidine (His). By processing the experimental data, it has been possible to obtain the complexation constants reported below.

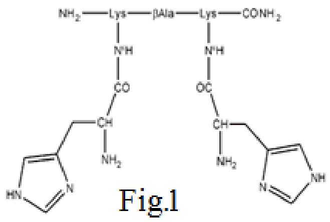

Fig.1

log (constant ± 3σ)

$Ga^{3+} + HHis^+ + 2H_2O = Ga(OH)_2His^+ + 3H^+$ −6.98 ± 0.09

$Ga^{3+} + H_5L^{5+} + 2H_2O = Ga(OH)_2H_3L^{4+} + 4H^+$ −9.69 ± 0.16

Spectroscopy data are in agreement with the potentiometric measurement. ^{1}H–NMR measurements conducted in H_2O as solvent at different metal/ligand ratio (0.0(A), 0.5(B), 1.0(C), 1.5(D)), indicate that imidazolic rings are involved in coordination with metal ions investigated (Fig.2). Distribution curves (in solution with 2.0×10^{-3} M in metal ion and ligand) show a wide range of pH (4–9) where Ga(III)–PHIS complex is the predominant specie (Fig.3).

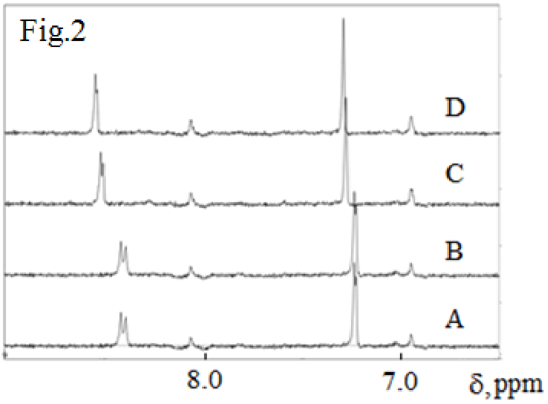

Fig.2

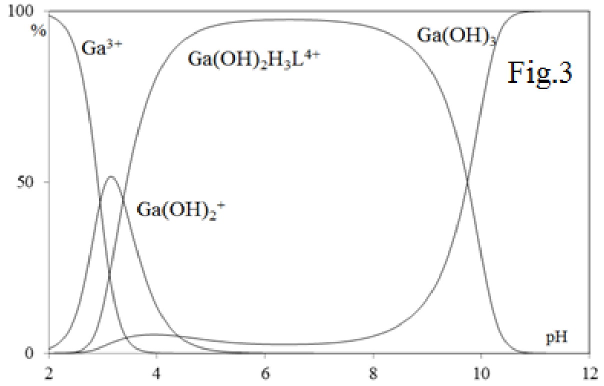

Fig.3

References

1. D'Andrea L. *et al.*; Peptide Science, 2008, 90(5), 707−712.
2. AlDeghaither, D.; Smaglo, B.G.; Weiner, L.M. Beyond, J. Clin. Pharmacol. 2015, 55(0 3), 4−20.

Structural Characterization of Bio-Functionalized Gold Nanoparticles By Ultrahigh Resolution Mass Spectrometry

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Bio-functionalized gold nanoparticles (AuNPs) have a vast field of applications. The unique properties of AuNPs functionalized with biomolecules such as peptides, proteins, lipids and carbohydrates enable innovative translational research and development in biomedicine. Current research focuses for example on the development of AuNPs for imaging, photothermal therapy, vaccination strategies and drug delivery. AuNPs in the 2-100 nm size range are typically synthesized in solution by redox reactions and can be functionalized by introducing molecules containing a thiol group to form a strong nanoparticle-sulfur bond. The structural characterization of functionalized AuNPs is challenging and requires the combination of multiple analytical techniques. Mass spectrometry (MS) has been successfully used to analyze AuNPs functionalized with small synthetic ligands with molecular mass smaller than 1000 Da. Laser desorption/ionization (LDI) and matrix-assisted LDI (MALDI) have been used in combination with time-of-flight (TOF) MS to analyzed ligands directly detached from the surface of AuNPs during the ionization process. However, TOF MS provides limited performance in terms of mass resolution and MS/MS possibilities. Thus, the analysis of AuNPs ligands has been limited to the determination of molecular mass only. To overcome these limitations, we designed an new strategy for the analysis of AuNPs based on ultrahigh resolution Fourier transform ion cyclotron resonance (FTICR) MS and a combination of LDI and MALDI. Following this strategy, we comprehensively characterized the surface chemistry of AuNPs conjugated via a thiol-ending linker to either the ovalbumin peptide (OVA 323-339), the Lewis X antigen (Galβ1-4[Fucα1-3]GlcNAcβ1) trisaccharide, the tetramannoside Manα1-2Manα1-2Manα1-3Manα1, or a mixture of both carbohydrates. We analyzed all bio-functionalized AuNPs by 15T LDI/MALDI-FTICR MS (Bruker) using 1,5-diaminonaphthalene (1,5-DAN) as a MALDI matrix. We used collision-induced dissociation (CID) to characterize the structure of pseudo-molecular ions generated by LDI/MALDI, in-depth. These included $[M+H]^+$ and $[M+Na]^+$, and importantly also $[M+Au]^+$ and $[M+2Au-H]^+$ ions which provide direct evidence for the Au-conjugation of ligands. In addition, we used our strategy to monitor proteolytic cleavage of peptides conjugated to the AuNP surface.

This study presents a novel application of ultrahigh resolution LDI/MALDI-(CID)-FTICR MS for the characterization of bio-functionalized AuNPs.

Molecularly Imprinted Materials Coupled to MALDI-TOF Mass Spectrometry for the Targeted Analysis of Peptides and Proteins.

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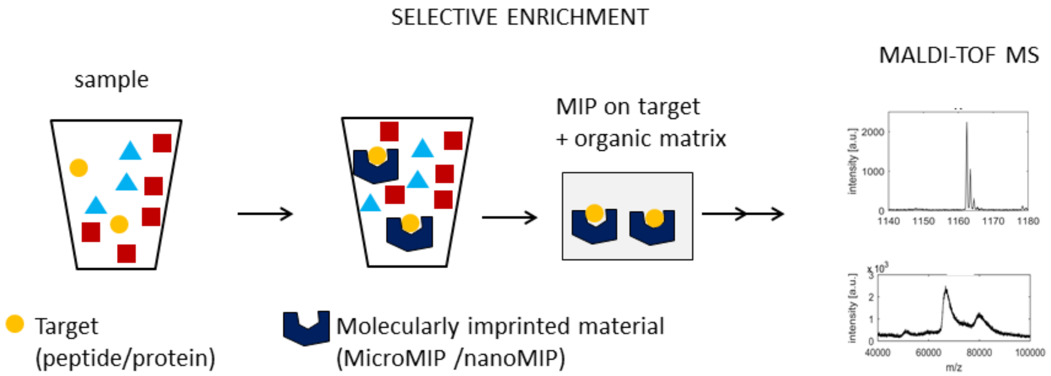
Molecularly imprinted polymers (MIPs) are a class of tailor-made biomimetic materials, prepared by template assisted synthesis: the monomers and the crosslinker are polymerized in the presence of the target analyte, called the template, thus printing onto the growing polymeric chains both the stereo and the chemical complementarity for the template. MIPs exhibit exceptional recognition properties for the template (being this a small molecule, a peptide or even a protein) with reported affinities and selectivity of the par of natural antibodies[1-3]

With the aim at improving the analytical methodologies meant for targeted proteomics and clinical applications, we propose the development of a flexible analytical platform based on the integration of MIPs to MALDI-TOF mass spectrometry (MS) for targeted protein analysis and characterized by selective enrichment,[4] high sensitivity and selectivity and short analysis times.

Libraries of micro and nano-MIPs addressed at the recognition of peptides and proteins, including responsive MIP-materials, were synthesized by radical polymerization of acrylamido-based monomers. The prepared materials were characterized physico-chemically, showing ~2 µm microMIPs and ~50 nm nanoMIPs. The MIP compositions were confirmed by XPS analysis. The binding isotherms demonstrated nanomolar affinities for the templates. At last, the micro- and nanoMIP materials were coupled to MALDI-TOF-MS.

The analytical performance of the MIP/MALDI-TOF-MS was studied by challenging the system with selected peptides and proteins, at concentrations spanning from the nano- to the pico-molar; in model solution and in real biological specimens.[5,6]

The results demonstrated the ability of the MIP/MALDI-TOF-MS hyphenation to detect in short times (few minutes) pico- to femto-moles of the target analyte straight from serum samples, with minimal sample handling, hence proving the strength of coupling micro- and nano-MIP materials to MALDI-TOF-MS, opening up innovative analytical perspectives.



References
1. Alexander C. et *al.*; J. Mol. Recognit. 19 (2003) 106–180.
2. Bossi et *al.*; Biosens. Bioelectronics 22 (2007) 1131-1137.
3. Hoshino Y. et *al.*; J. Am. Chem. Soc. 130 (2008) 15242–3.
4. Urban P. L. et *al.*; Mass Spectrom. Rev. 30 (2011) 435–478.
5. L. Cenci et *al.*; *J. Mol. Recognit*., 2016, 29, 41–50.
6. Bertolla et *al.*; *ACS Appl. Mater. Interfaces*, 2017, *9*, 6908−6915.

Unknown And Non-Target Analysis To Determine Pesticides In Fruit And Vegetables By Means Of UHPLC-HRMS (Orbitrap)

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In the last years, high-resolution techniques have enhanced the number of pesticides and pesticide-related metabolites that can be detected in food. Conventionally, the detection of pesticides in food by means of both non-target and unknown screening methods has been accomplished by either GC-HRMS or LC-HRMS followed by data processing with specific, but limited, compound databases developed by companies working in the field[1]. Empirical formulas of the molecules under investigation can be generated through a combination of parameters such as mass accuracy, isotopic clusters and ion fragments in order to be used for researches on online databases (e.g. ChemSpider).
This work reports a chromatographic-alignment mass-spectrometry-based approach to detect and identify pesticides and pesticide-related metabolites by comparison of matrix blank chromatograms ("CONTROL") with unknown sample chromatograms ("SAMPLE").
An UHPLC/Orbitrap system was used to carry out five chromatographic runs of both blank matrices (CONTROL) and sample matrices (SAMPLE) and a single FullScan-ddSM^2 chromatographic run.
The software calculated a SAMPLE to CONTROL *ratio* taking the average intensity of signals originated from unknown sample chromatograms and the signals originated from matrix blank chromatograms. SAMPLE/CONTROL ratios and p-values calculated on the SAMPLE signals were used to establish a threshold to filter out non-significant values. The unknown pesticides were then identified referring to online databases such as ChemSpider/Pesticides common Names, EPA Toxcast and FDA.
A specific software was used to confirm suggested compound identities and structures based on observed fragmentation patterns. All metabolites and/or degradation products of pesticides that can possibly be found in the samples can be investigated after identification through the method described above.
Quality control approach to test this method was made using SANTE/11945/2015 document as reference. A team of research unrelated to this experiment spiked samples of stone fruits with 36 different pesticides showing a wide range of physical-chemical properties thereby ensuring all compound classes detectable by LC-MS to be represented.
This method was compared to both a screening target method that uses a 350 compounds homemade database with 350 compounds and non-target method that uses a database with 650 pesticides from.
The results provided an unambiguous identification and structural characterization of the compounds based on accurate mass measurement and informative fragmentation spectra resulting in no false positive and no false negative data. Moreover, this method allowed to detect and identify two metabolites undetected by both target and non-target approach.

References
1. Masiá, A., Suarez-Varela, M.M., Llopis-Gonzalez, A., Picó, Y.; "Determination of pesticides and veterinary drug residues in food by liquid chromatography-mass spectrometry: A review"; *Analytica Chimica Acta*, 2016, *936*(14), 40-61.

From Ascorbic Acid to Furan molecules: A Theoretical and Experimental study on the Gas Phase Acid Catalyzed degradation of Vitamin C

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Degradation of L-ascorbic acid (L-AA) occurs into two types of reactions, named the non-oxidative and the oxidative. The main difference between these two pathways is that furfural is more easily produced through the former. It should be noted that the expression non-oxidative refers solely to the nature of the initial step, since subsequent transformations may involve various oxidation steps. Indeed, the oxidative pathway describes the reaction which involves as an initial step the oxidation of L-ascorbic acid to dehydro-L-ascorbic acid. Likewise, the non-oxidative pathway relates to the direct decomposition of L-ascorbic acid with exclusion of dehydro-L-ascorbic acid as an intermediate structure. In 1995, furan and its derivatives were classified by the International Agency on Cancer Research (IARC) in the group 2B, as possibly carcinogenic to humans.

Since the first report in 1933, the formation of furfural from L-AA in strong acid media has been confirmed by many workers and some reaction mechanisms for the formation of furfural from L-AA have been proposed. However, none of them seems to be acceptable as the mechanism taking place in ordinary food stuffs.

Here we report on the gas-phase investigation performed by a joined mass spectrometric and theoretical approach on the acid catalysed mechanism for the formation of furan compounds in the non-oxidative degradation of L-AA. According to this approach, gaseous protonated ascorbic acid ions, $[C_6H_8O_6]H^+$, at m/z 177, were generated by Electrospray Ionization Mass Spectrometry of an ascorbic acid solution. The $[C_6H_8O_6]H^+$ ionic reactants at m/z 177 were previously structurally characterized as the ascorbic acid molecule protonated at the O2 carbonyl oxygen atom[1].

They were subjected to collisionally activated decomposition (CAD) in order to induce the gas phase unimolecular degradation pathway of protonated ascorbic acid.

The degradation pathway emerging from the CAD mass spectrum of the precursor ion at m/z 177 shows a twofold dehydration step, 177→159 and 159→141 followed by the elimination of an $HCOOH/CO_2$ moiety, 141→95/97, leading to the formation of furanic products.

Energy Resolved CAD mass spectra allowed to obtain informations on the relative energies of degradations steps. Experimental results were compared with those of a theoretical investigation performed at B3LYP/6-31+G(d,p) level of theory highlighting the most favourable decomposition pathway. The mechanism leading to furan compounds involves dehydration, hydrolysis of the lactone ring followed by decarboxylation.

Reference
1. Ricci A, Pepi F, Cimino P, Troiani A, Garzoli S, Salvitti C, Di Rienzo B, Barone V. *"Vitamin C: an experimental and theoretical study on the gas-phase structure and ion energetics of protonated ascorbic acid"* J Mass Spectrom. 2016 51(12):1146-1151. doi: 10.1002/jms.3848.

Liquid-EI (LEI) Atmospheric Pressure Mechanism for the introduction of liquid streams into an unmodified electron ionization source of a mass spectrometer.

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We have combined, for the first time, an atmospheric pressure gas-phase conversion mechanism with new ceramic coatings to create an innovative interface, called Liquid-EI (LEI) (1). LEI is based on electron ionization (EI) but differs from previous attempts; the vaporization of solutes and mobile phase takes place at atmospheric pressure into a specifically designed region, called the "vaporization micro-channel", before entering the high-vacuum ion source. The interface is completely independent from the rest of the instrumentation, and can be adapted to any gas chromatography-mass spectrometry (GC-MS) system, as an add-on for a rapid LC-MS conversion. A ceramic liner, placed inside the vaporization micro-channel, acts as an inert, 'non-stick' vaporization surface, speeding up the gas-phase conversion of large molecules while lessening possible memory effects.

EI is an unparalleled, well-established tool for the identification of unknown gas-phase molecules. Its extension to a liquid phase, without the drawbacks and limitations that troubled this hybrid combination to date, provide the same unique advantages (library searchable mass spectra, robustness, negligible matrix effects) to LC amenable compounds, opening the door to new, challenging LC-MS applications. Deactivated silica coatings help to release the heaviest compounds to the gas-phase, improving vaporization efficiency and reducing high-temperature contact time for the most labile substances, bridging the gap between the world of classic LC-MS and GC-MS.

References
1. Termopoli, V., Famiglini, G., Palma, P., Piergiovanni, M., Cappiello, A. *Anal Chem* (2017) 89 (3), pp 2049–2056.

Selective gas-phase conversion of D-fructose to 5-hydroxymethylfuraldehyde through a base-assisted dehydration process

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5-hydroxymethylfuraldehyde (5-HMF) is the main product of the thermal acid-catalysed dehydration of monosaccharides and together with other furan compounds is considered a platform molecule for the production of chemicals and fuels. Identifying alternative catalytic strategies to synthesize 5-HMF represents a key-step to increase reaction selectivity and reduce degradation-by-product yields. In this regard, mass spectrometry has proved to be an useful tool for studying reaction mechanisms in absence of solvent molecules. This approach has already been employed to investigate the acid-catalysed D-glucose and D-fructose dehydration mechanism, highlighting the formation in the gas-phase of a 5-HMF protomers and isomers mixed population (1,2). In this work the effect produced by nitrogen-containing bases on the D-fructose dehydration reaction has been evaluated using tandem mass spectrometry. Ionic complexes formed by the protonated sugar and a nitrogen base were allowed to undergo collision-induced dissociation (CID) in an ion trap mass spectrometer. The dehydration process was followed step-by-step by isolating in turn the resulting ionic intermediates that still retain the attached bases depending on their proton affinity values. The sequential fragmentation leads to the formation of $[C_6H_6O_3]H^+$ ions corresponding to a pure protonated 5-HMF population when the base loss occurs as the last reaction event (Figure 1). This evidence demonstrates the existence of a selective and effective base-assisted mechanism. Theoretical calculations are in progress in order to: i) elucidate the structures of the starting reactant ion and of the intermediates ii) validate a feasible reaction mechanism.

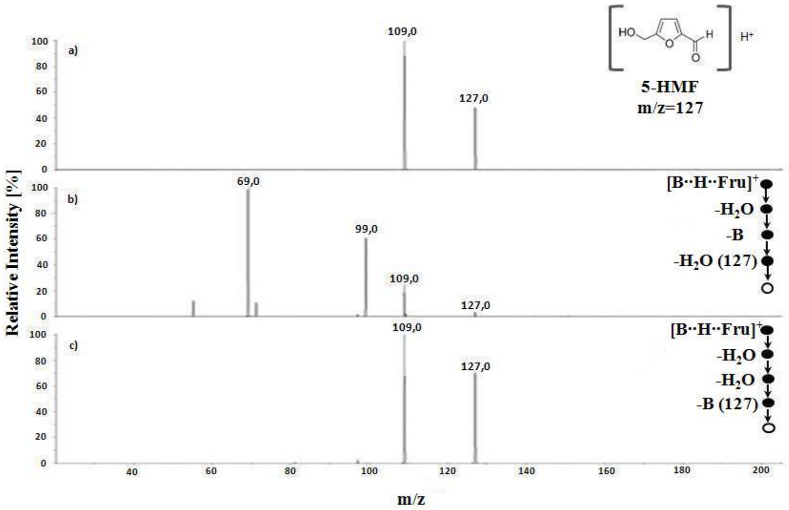

Fig. 1 CID mass spectra of a) protonated standard 5-HMF, b) ions at m/z 127 obtained after a premature base loss and c) ions at m/z 127 arising when the base loss occurs as the last reaction event.

References
1. A. Ricci, B. Di Rienzo, F. Pepi, A. Troiani, S. Garzoli, P. Giacomello, *J. Mass Spectrom.* **2015**, *50*, 228-234
2. F. Pepi, A. Ricci, S. Garzoli, A. Troiani, C. Salvitti, B. Di Rienzo, P. Giacomello, *Car. Res.*, **2015**, *413*, 145-150.

Development of a new platform for chemical sensors based on surface plasmon resonance and molecularly imprinted polymers as receptors

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Optical sensors based on POF have some advantages over those based on different waveguides, as for example the prism of the classical Biacore instrument. One of them, particularly relevant, is the possibility of remote sensing. A problem could be the integration of the receptor with the fiber, for which different strategies have been proposed[1]. Particularly useful seems to be a platform recently proposed by our group[2], consisting in a D-shaped plastic optical fiber without cladding, in contact with a thin gold layer. The fiber is maintained in a fixed and stable position by a small cubic holder purposely designed. The artificial receptor, i.e. the molecularly imprinted polymer, is deposited over the gold layer, so that it constitutes the dielectric medium whose refractive index determines the plasmon resonance effect. In the present investigation a new sensor platform, based on surface plasmon resonance (SPR) phenomenon (based on a slab waveguide and two POFs), is presented. In this case the waveguide for SPR is a thin chip of the same material of the optical fiber core (PMMA), not the optical fiber itself. The optical fiber is used to introduce the light into the slab waveguide, exploiting the evanescent wave phenomenon, and to translate the light emerging from the waveguide to the spectrometer (see Figure 1). A thin gold layer (60 um) is deposited over the PMMA chip (slab waveguide), and the molecularly imprinted polymer is deposited over it. This operation is relatively easy to perform, due to the flat shape of the gold surface. Other advantages of this new approach are the possibility of sensing with a removable chip, the easy production of an engineered platform and the use of a new holder, which is also suitable for thermo-stabilized flow cell in chemical sensing applications.

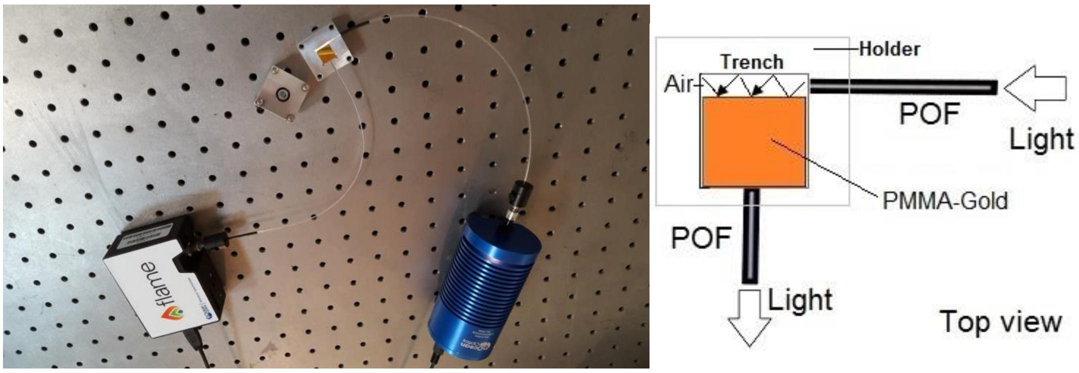

Figure 1. Experimental setup of the sensor system

It has been found that the performances obtained by this configuration are very similar to those obtained by the previously proposed platform (2). In particular, the optical sensitivity and the resolution are similar, being respectively 1500 nm/RIU and 10^{-3} RIU. These preliminary results showed that the sensor's performances make it suitable for chemical applications.

References
1. R. K. Verma, A. K. Sharma, B. D. Gupta, IEEE Photonics Technology Letters, 2007, 19, 1786-1788.
2. N. Cennamo, G. D'Agostino, R. Galatus, L. Bibbò, M. Pesavento, L. Zeni, Sensors and Actuators B, 2013, 188, 221–226.

Enantioselective voltammetry on achiral electrodes: a comparison between inherently chiral additives based on different stereogenic elements

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An attractive target in electroanalysis is the availability of chiral media affording enantioselection in terms of significant peak potential difference between the antipodes of chiral probes in voltammetry experiments on achiral electrodes. Previous literature attempts pointed to enantioselectivity increasing with the structural order of the chiral medium; on the other hand, outstanding enantioselection performances have been recently observed working on electrode surfaces consisting in "inherently chiral" oligomer films, that is, in which chirality does not originate from localized stereocenters, but is intrinsic of the whole main molecular backbone, featuring a tailored torsion[1-5]. Combining both strategies we have recently developed two inherently chiral ionic liquids ICILs, consisting of dialkylated bicollidinium salts, with an atropoisomeric bipyridinium cation featuring at least one octyl chain and bistrifilimide counteranions. They showed high enantioselectivity when tested even as low concentration additives in commercial achiral ionic liquid media[6]. Importantly, similar ability was also shown by other terms of the same family, having shorter alkyl chains and/or different counteranions, solid at room temperature but of easier synthesis. As a first temptative explanation we are considering the high supramolecular order of even simple ionic liquids at the interphase with a charged surface. A chiral additive could result in chiral reorganization of this peculiar interphase, as in the case of nematic-to-cholesteric transitions induced by chiral dopants in liquid crystals[6]. Such application of the chiral selector as additive in an achiral ionic liquid rather than as the bulk medium is indeed interesting and convenient, since only a small quantity of the enantiopure selector is needed and a low melting point is no more required, but only sufficient solubility in the achiral ionic liquid. This allowed us to include in our chiral voltammetry experiments a quite larger number of inherently chiral selectors based on different stereogenic elements, *i.e.*, the bicollidine and bibenzimidazole atropoisomeric scaffolds and the tetrathielicene helicoidal scaffold. They all proved successful. Large potential differences were observed on achiral electrodes for the enantiomers of chiral probes even of very different structure and electroactivity, as in the former tests on inherently chiral electrodes, and possibly even in experiments with more than one probe, providing further evidence of the general validity of the "inherent chirality" strategy in the development of efficient chiral selectors in electroanalysis.

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References
1. *Angew. Chem. Int. Ed.*, 2014, 53, 2623.
2. *Chem. Eur. J.*, 2014, 20, 15298.
3. *Chem. Sci.*, 2015, 6, 1706.
4. *Chem. Eur.*, 2016, 22, 10839.
5. Anal. Bioanal. Chem., 2016, 408, 7243.
6. *J Angew. Chem. Int. Ed.*, 2017, 56, 2079.

Hydrogen peroxide sensitive and selective biosensors based on peroxidases from different sources wired by Os-polymer

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A comparison has been made between two plant peroxidases, cationic horseradish peroxidase (HRP) and anionic tobacco peroxidase (TOP) (1), to form the basis together with a highly cationic osmium polymer [Os(4,4′-dimethyl-2,2′-bipyridine)$_2$poly(N-vinylimidazole)$_{10}$Cl]$^{+2/+}$ ([Os(dmp)PVI]$^{+/2+}$) (2) to prepare highly sensitive, stable and selective hydrogen peroxide biosensors (3). The two different plant peroxidases were individually immobilized onto graphite rod (G) electrodes by a three steps drop-casting procedure consisting of the subsequent deposition of an aqueous solution of ([Os(dmp)PVI]$^{+/2+}$), followed by a solution of poly(ethyleneglycol) diglycidyl ether (PEGDGE), used as a cross linking agent and finally an aliquot of a solution of anionic HRP or cationic TOP to make HRP/PEGDGE/[Os(dmp)PVI]$^{+/2+}$/G and TOP/PEGDGE/[Os(dmp)PVI]$^{+/2+}$/G based electrodes, respectively (4). Electrochemical experiments were carried out to investigate the influence of the surface charge of the enzyme and the charge of the polymer on the efficiency of the electron transfer (ET) between the enzyme and the wiring redox polymer and the efficiency for electrocatalytic reduction of H_2O_2. In the case of HRP a decrease in the ET rate was observed due to the repulsion between this enzyme and the polymer, both positively charged, whereas with TOP there was an enhanced ET rate due to the attraction between the anionic enzyme and the cationic polymer. The effects of enzyme loading and pH were investigated. Both optimized peroxidase modified electrodes exhibited a wide dynamic response range (1-500 μM H_2O_2) and a low detection limit (0.3 μM H_2O_2). The TOP based electrode showed a higher sensitivity (467.4 nA μM^{-1} cm^{-2}) compared to that of the HRP based electrode (297.1 nA μM^{-1} cm^{-2}) and an improved long-term stability (decrease in 17.3% upon 30 days). Both enzyme electrodes showed a response time of 3 s. The HRP based sensor was more sensitive to the presence of phenolic compounds acting as alternative electron donors whereas the TOP based sensor was virtually interference free. Both HRP and TOP based electrodes were successfully tested in contact lens cleaning samples and real "spiked" samples from different sources such as tap water, milk and dairy products.

References

1.I.G. Gazaryan, L. Gorton, T. Ruzgas, E. Csöregi, W. Schuhmann, L.M. Lagrimini, D. Khushpulian, V.I. Tishkov, Tobacco Peroxidase as a New Reagent for Amperometric Biosensors, J. Anal. Chem. 60 (2005) 558-566.
2.R. Antiochia, L. Gorton, A new osmium-polymer modified screen-printed electrode for fructose detection, Sens. Act. B 195 (2014) 287-293.
3. M.G.C. Baldry, The bactericidal, fungicidal and sporicidal properties of hydrogen peroxide and peracetic acid, J. Appl. Bacter. 54 (1983) 417-423.
4. S. Gaspar, K. Habermüller, E. Csöregi, W. Schuhmann, Hydrogen peroxide sensitive biosensor based on plant peroxidases entrapped in Os-modified polypyrrole films, Sens. Act. B, 72 (2001) 63-68.

Seasonal variations of major phospholipids in mussels of sp. *Mytilus galloprovincialis*: an investigation by hydrophilic interaction liquid chromatography-electrospray ionization Fourier-transform mass spectrometry

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Mytilus galloprovincialis, also known as *Mediterranean mussel*, is one of the most commercially relevant species belonging to the genus *Mytilus*. With more than 500 ktons per year its production represents the top shellfish-oriented aquaculture activity in Europe (1). Since *M. galloprovincialis* is mainly commercialized as alive/fresh product, thus having a few days of shelf life, its availability on the market is naturally subjected to seasonal fluctuations, usually due to three synergic factors: breeding technique, natural recruitment of juveniles and reproductive cycle. The latter, as well as mussel biochemical composition, is known to be strongly influenced by water temperature and food availability, in turn related to season and geographical area, since mussels are a typical product of non-fed aquaculture, thus their feeding depends on the natural availability of nutrients (2). The effects of environmental temperature on the viability of cultured mussels have been dramatically confirmed by the massive loss of production, and the consequent economical damage, occurred in several Italian aquacultural plants in July 2015, because of a prolonged heat wave, finally leading sea temperatures to rise up to 35 °C. In the perspective of a worsening of environmental conditions due to global warming, the monitoring of mussel viability through appropriate molecular markers could be very useful to contain such losses in case of sea water over-heating, e.g. by moving the production to naturally colder basins, when possible. Recently, high efficiency hydrophilic interaction liquid chromatography (HILIC) and high resolution/accuracy electrospray ionization – Fourier-transform mass spectrometry (ESI-FTMS) have been exploited for the systematic characterization of *lyso*-phospholipids in mussel lipid extracts, showing their correlation with thermal stresses occurring on mussels (3). Starting from these premises an extended characterization of the two main classes of mussel phospholipids (PL), namely phosphatidylcholines (PC) and phosphatidyl-ethanolamines (PE), has been undertaken to verify how seasonal variations may affect their profile and, consequently, if lipid species can be considered indirect markers of changing sea temperatures as a result of adaptation of mussels to adverse environmental conditions. So far more than 300 different compounds, namely 185 PC and 131 PE, have been recognized, including plasma(e)nylic species, i.e. PL bearing one of the side chains linked to glycerol through an ether bond, that were the prevailing species among PE. Their characterization by HILIC-ESI-FTMS analysis will be described in the present communication. Moreover, the specific differences between PC and PE profiles of mussels collected in different seasons, emphasized by a chemometric approach, will be discussed.

References
1. European Commission, *Fisheries and aquaculture in Europe*, 2012, 59, 8.
2. M.P. Suárez, C. Alvarez, P. Molist, F. San Juan, *J. Shellfish Res.*, 2005, 24, 531-540.
3. L. Facchini, I. Losito, C. Cianci, T.R.I. Cataldi, F. Palmisano, *Electrophoresis*, 2016, 37, 1823-1828.

Applications of Porous Graphitic Carbon in Liquid Chromatography – Mass Spectrometry

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The remarkable improvements in hyphenated analytical methods over the last two decades have significantly broadened their applications however, in several important cases, the interfacing of separation techniques with mass spectrometry still suffer of poor compatibility. Among different approaches, porous graphitic carbon (PGC) is a HPLC stationary phase which appear especially appropriate for small ions or neutral polar compounds scarcely retained by reversed phases[1] nevertheless, in spite of its attractive peculiar characteristics, the use of porous graphitic carbon (PGC) never took off in standard environmental and bio-analytical labs. A possible reason for it lies in the complexity of its dual behavior[2]. PGC, in fact, provides a mixture of interactions[3], both strongly hydrophobic and electronic[4], thus making difficult the predictions regarding its retention ability. Another possible reason for the "underuse" of this stationary phase is that many components of environmental or biological samples can be strongly adsorbed on it suddenly modifying the retention characteristic of the column[5]. This might result in the need for an additional column washing and reconditioning procedure. Nevertheless, several challenging separations of ionic or highly polar and hydrophilic compounds can benefit of PGC retention abilities and its excellent selectivity[6,7]. The results of several studies devoted to outline general use guidelines for PGC in combination with ESI-MS detection will be presented and the performances compared with those of ion chromatography (IC), classic reversed phase (RP) and hydrophilic interaction chromatography (HILIC).

References

1. L. Pereira, "Porous Graphitic Carbon as a Stationary Phase in HPLC: Theory and Applications"; *Journal of Liquid Chromatography & Related Technologies*; 2008, *31*, 1687–1731.
2. C.K. Lim, Chapter 1, "Liquid Chromatography in Biomedical Analysis: Basic Approach"; in: T. Hanai (Ed.), *Journal of Chromatography Library*, Elsevier, 1991.
3. E. Forgács, "Retention characteristics and practical applications of carbon sorbents", *Journal of Chromatography A;* 2002, *975*, 229–243.
4. T. Hanai, "Separation of polar compounds using carbon columns"; *Journal of Chromatography A*; 2003, *989*, 183–196.
5. T.E. Bapiro, F.M. Richards, D.I. Jodrell, "Understanding the Complexity of Porous Graphitic Carbon (PGC) Chromatography: Modulation of Mobile-Stationary Phase Interactions Overcomes Loss of Retention and Reduces Variability"; *Anal. Chem.*; 2016, *88*, 6190–6194.
6. E. Holmgren, H. Carlsson, P. Goede, C. Crescenzi, "Determination and characterization of organic explosives using porous graphitic carbon and liquid chromatography–atmospheric pressure chemical ionization mass spectrometry", *Journal of Chromatography A;* 2005, *1099*, 127–135.
7. M. Rodriquez, D.S. Cretoso, M.A. Euterpio, P. Russo, C. Crescenzi, R.P. Aquino, "Fast determination of underivatized gentamicin C components and impurities by LC-MS using a porous graphitic carbon stationary phase"; *Anal. Bioanal. Chem.*; 2015, *407*, 7691–7701.

Synthetic Receptors for Troponin T Detection by SPR Transduction for Acute Myocardial Infarction Diagnosis

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Acute Acute myocardial infarction (AMI) is a prominent cause of mortality worldwide with a very high economic impact[1]. Currently, cardiac Troponin (cTn) isoforms I and T are the preferred diagnostic biomarkers of myocyte necrosis because when the heart cells are damaged this protein is quickly released into the bloodstream and its early detection can improve the survival rate[1,2]. Among the several methods used for cardiac biomarkers detection, affinity-based biosensors appear the most promising, due to mandatory demand of fast and reliable answer upon recognition of target molecules with high specificity. In this framework, we report the outcomes of our research dealing with the development of biosensing platforms based on SPR (Surface Plasmon Resonance) transduction. In particular, the detection of the cardiac biomarker cTnT by testing emerging synthetic receptors alternative to antibodies[3], like aptamers (oligonucleotides <100mer)[4], and MIPs (Molecularly Imprinted Polymers)[5] is here presented. These biomimetic have been already successfully exploited for numerous biosensors applications, including electrochemical methods for cTnT detection[6,7,8]. Here we report for the first time their perspective use for optical-based biosensing.

For this purpose, several target recognition strategies have been designed and investigated to enhance the system performance, in terms of sensitivity, selectivity and reproducibility for this point-of-care approach with promising social and economic beneficial impact.

References

1. G.W. Reed, J.E. Rossi, C.P. Cannon, “Acute myocardial infarction”; *The Lancet*, 2017, *389*, 197-210.
2. A.S. Go et *al.*, “Heart Disease and Stroke Statistics”; *Circulation*, 2013, *127*, e6-e245.
3. M. Abdolrahim, M. Rabiee, S.N. Alhosseini, M. Tahriri, S. Yazdanpanah, L. Tayebi, “Development of optical biosensor technologies for cardiac troponin recognition”; *Analytical Biochemistry*, 2015, *485*, 1-10.
4. S. Tombelli, M. Minunni, M. Mascini, “Analytical applications of aptamers”; *Biosensors and Bioelectronics*, 2005, *20*, 131-144.
5. L. Uzun, A.P.F. Turner, “Molecularly-imprinted polymer sensors: realising their potential”, *Biosensors and Bioelectronics*, 2016, *76*, 2424-2434.
6. S. Campuzano, P. Yáñez-Sedeño, J.M. Pingarrón, “Diagnostics Strategies with Electrochemical Affinity Biosensors Using Carbon Nanomaterials as Electrode Modifiers”; *Diagnostics*, 2017, *7*, 1-26.
7. N. Karimian, A.P.F. Turner, A. Tiwari, “Electrochemical evaluation of troponin T imprinted polymer receptor”; *Biosensors and Bioelectronics*, 2014, *59*, 160-165.
8. N. Karimian, M. Vagin, M.H.A. Zavar, M. Chamsaz, A.P.F. Turner, A. Tiwari, “An ultrasensitive molecularly-imprinted human cardiac troponin sensor”; *Biosensors and Bioelectronics*, 2013, *50*, 492-498.

Nano- and Micro-particles in Food and Consumer Products: the Role of the Field Flow Fractionation Techniques in Their Characterization

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Nanomaterials (NMs) cover a broad range of materials of different chemical composition. Because of their diverse properties, they are used in a wide range of applications and products, such as cosmetic products (e.g. UV absorbers in sunscreens), food (enhanced flavour and texture, encapsulation of micronutrients), medical devices (diagnostics, drug delivery), medicinal products.
The recent abundant use of NMs has placed, however, the accent on their potential risk, since nanoparticles, with their sizes between 1-100 nm, might interact with membrane cells of any living beings (plants, animals, humans). Consequently, legislators who are dealing with health and consumer protection have asked to the scientific community to implement or set-up new analytical methods able to detect and characterize the nanoparticles contained especially in food and consumer products to evaluate the risk on a solid definition of NMs.
This work will illustrate, as the Field Flow Fractionation techniques (FFF), might be useful separation instruments to sort complex samples[1] and to determine the average sizes and the particle size distribution of nano- and micro-particles. FFF techniques are often coupled online with a series of detectors such as UV-vis, refractive index, fluorescence, scattering detectors (DLS or MALS), ICP-MS, ICP-OES, GFAAS, whose choice depends on the practical application.
Examples of SiO_2, silver, and ZnO separations will be presented in the light of the characterization suggested by the European Commission[2].

References
1. M.E. Schimpf, K.D. Caldwell, J.C. Giddings, "Field-Flow Fractionation Handbook"; *Wiley-Interscience*, New York, 2000.
2. T. Linsinger, G. Roebben, D. Gilliland, L. Calzolai, F. Rossi, N. Gibson, C. Klein, "Requirements on measurements for the implementation of the European Commission definition of the term "nanomaterial"; *JRC*, 2012.

Evaluation and Comparison of Gel-based and Gel-free Approaches for the In-depth Exploration of Milk Rice Proteome

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Nowadays a growing number of consumers opt for plant-based milk substitutes for medical reasons (such as lactose intolerance and cow's milk allergy) or as a lifestyle choice[1]. Also, in countries where mammal milk is scarce and expensive, plant milk substitutes serve as a more affordable option. Among the plant milk there is milk extracted from rice. Rice milk is made from boiled rice (both brown and white rice versions are available), and it is often supplemented with flavour enhancers like brown rice syrup and vanilla to help it taste more like cow's milk. Interestingly, it has been reported that rice milk represents a better alternative than soy milk for infants allergic to cow's milk. However, despite the known benefits and potential of rice milk, a detailed characterization of its protein content is needed.

In this study, in order to provide the most complete characterization of the proteins contained in the rice milk we have evaluated and compared different gel based and gel free proteomic approaches. In particular, we compared the results obtained from LC-MS/MS analysis after protein precipitation with acetone or TCA, or after protein prefractionation based on SDS-PAGE (GeLC-MS/MS) or ProteoMiner™, or after prefractionation based on peptide IEF (pIEF-LC-MS/MS)[2]. We also estimated the abundance of the identified proteins by using the exponentially modified protein abundance index (emPAI). Overall, a total of 158 different protein species based on a total of 585 peptides have been identified for the first time in the rice milk. Interestingly, the results obtained show that applying peptide IEF can significantly increase the number of proteins identified from rice milk. We also demonstrated that the rice milk proteome contains proteins mainly characterized by a Mw between 10 and 70 kDa and acidic pI, with approximately 55% of the identified proteins within the range of pI 5.0–7.0. Moreover, most of the identified proteins showed a negative GRAVY index, confirming the prevalence of hydrophilic proteins in plant milk. The identified proteins were also grouped into cellular roles based to Gene Ontology annotation according to molecular function, biological process, and cellular component. In particular, catalytic activity (56%) and metabolic process (41%) are the two most representative categories of this milk proteome. In conclusion, we demonstrate that efficient fractionation of peptides by IEF is an essential prerequisite for comprehensive analysis of protein mixtures by shotgun mass spectrometry, and more specifically for a complete characterization of the milk rice proteome.

References
1. O.E. Makinen, V. Wanhalinna, E. Zannini, E.K. Arendt; *Crit Rev Food Sci Nutr*, 2016, *56*, 339-49.
2. R. Millioni, C. Franchin, P. Tessari, R. Polati, D. Cecconi, G. Arrigoni; *Journal of Chromatography A*, 2013,*1293*,1-9.

Aromatic Amines in Textile as Potential Threat for Human Health

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Possible chemicals found in textile samples have various sources or are added with different purposes. Pesticides can for instance be used in the production step of natural fabrics[1], added as repellent during the storage[2], or applied in anti-bug clothes improving the technical characteristics[3]. However, the main chemical source in common textile samples is the colouring step when the dyes are added. Depending on the purity, remaining reaction reagents can be present as dyes impurities[4], or parts of the dye structure can be released on the human skin by azo reduction of anaerobic bacteria[5].

In vivo experiments showed that a flame retardant, impregnated in sleepwear, can migrate from the fabric to the skin and further into the human body, since its metabolite could be detected in the subject's urine samples[6]. In our previous studies on different kind of textiles consumer product several highly toxic compounds were detected[7,8]. Among them we decided to focus on benzothiazole and its derivatives since is one of the most frequently detected compound. In another study of human skin excretions, was detected in some samples from the skin surface[9]. For this reasons, in order to assess the risk of benzothiazoles migration from worn clothes into and through the human, we have made transdermal diffusion tests on a synthetic, non-animal based model membrane using Franz cells.

References
1. B. Zhang; *Talanta*, 2008, *75*, 1055–1060.
2. J.M.A. Thompson; *Routledge*, 2015.
3. I. Holme; *Coloration Technology*, 2007, *123*, 59–73.
4. K. Hunger; *KGaA*, 2002, pp. 13–112.
5. F.J. Cervantes; *Rev. Environ. Sci. Biotechnol.*, 2011, 10, 125–137.
6. A. Blum; *Science*, 1978, *201*, 1020–1023.
7. R. Avagyan; *Environmental Science and Pollution Research*, 2015, *22*, 5842–5849.
8. G. Luongo; *Journal of Chromatography A*, 2016, *1471*, 11–18.
9. M. Gallagher; *Br J Dermatol.*, 2008, *159*, 780–791.

A Greener Approach for Organophosphate Flame Retardant Determination in Airborne Particulate Matter: Microwave-assisted Extraction Using Hydroalcoholic Mixture Coupled with Solid Phase Microextraction Gas Chromatography Tandem Mass Spectrometry

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Organophosphate esters (OPEs) are compounds widely used as flame retardants and plasticizers in different types of materials. Due to their extensive use, they have become ubiquitous pollutants in both outdoor and indoor environments[1,2,3].

In this work, a new analytical method for OPEs quantification in airborne particulate matter (PM) was developed. The proposed protocol provides for the microwave-assisted extraction (MAE) of the analytes from the PM followed by solid phase microextraction gas chromatography tandem mass spectrometry determination (SPME-GC-MS/MS). Ten organophosphate esters were taken into account i.e., tripropyl phosphate (TPP), tri-n-butyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP), tris(chloropropyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tributoxyethyl phosphate (TBEP), triphenyl phosphate (TPhP), 2-ethylhexyl-diphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP) and tricresyl phosphate (TCP). OPEs have been usually extracted from particulate matter by using traditional approaches including soxhlet[3] and ultrasonic extraction[4] with hexane, acetone or more toxic chlorinated solvents.

In the developed method, the OPEs were extracted by MAE using a green hydroalcoholic mixture composed of water and ethanol. Design of Experiment (DoE) was used for the multivariate optimization of the parameters affecting both the MAE extraction and the SPME analysis. A 2^{5-1} fractional factorial design was performed in order to determine the factors of the MAE that have a significant influence on the analyte extraction. Later on, the most important variables were further optimized by central composite design (CCD), thereby achieving the optimal working conditions. The extraction performance of five SPME fibers was evaluated. The DVB/CAR/PDMS coating demonstrated to be the most suitable for the extraction of the target analytes. The factors affecting the SPME extraction (i.e., extraction time, extraction temperature and ionic strength of the sample) were optimized by CCD. The optimal working condition determined by using Derringer's desirability function were 45 min as extraction time, 80°C as extraction temperature and 10.0% (w/w) of NaCl. The assay of the analytes was performed by using tandem mass spectrometry in selected reaction monitoring (SRM) acquisition mode. The proposed method was carefully validated. Satisfactory values were achieved in terms of linearity, accuracy, precision (Intra- and inter- day) and limit of quantification.

References

1. T. Reemtsma et *al.*; "Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate"; *TrAC-Trends Anal. Chem.*, 2008, vol. *27*, no. 9, pp. 727.
2. I. van der Veen and J. de Boer, "Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis"; *Chemosphere*, 2012, vol. *88*, no. 10, pp. 1119.
3. R. Suhring et *al.*, "Organophosphate esters in Canadian Arctic air: Occurrence, levels and trends"; *Environ. Sci. Technol.*, 2016, vol. *50*, no. 14, pp. 7409.
4. A. Marklund, et al. "Screening of organophosphorus compounds and their distribution in various indoor environments"; *Chemosphere*, 2003, vol. *53*, no. 9, pp. 1137.

Ultrasound-Vortex-Assisted Liquid-Liquid Micro-Extraction for Simultaneous Determination of Organophosphorus Pesticides and Phthalates in Baby Foods

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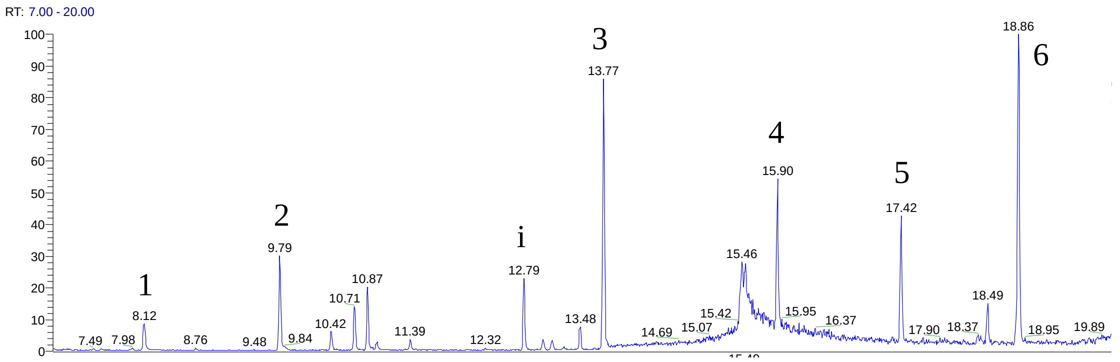
Baby food is any soft, easily consumed food, other than breastmilk or infant formula, that is made specifically for babies, roughly between the ages of four to six months and two years. The food comes in multiple varieties and tastes. The primary consumers of baby food, generally meets or significantly exceeds the recommended amount of macronutrients.

Baby foods are either a soft, liquid paste or an easily chewed food since babies lack developed muscles and teeth to effectively chew. Babies typically move to consuming baby food once nursing or formula is not sufficient for the child's appetite. Homemade baby food is less expensive than commercial baby foods. Homemade food is appropriate only when the family has a sufficient and varied diet, as well as access to refrigeration and basic sanitation. It is important to follow proper sanitation methods when preparing homemade baby food such as washing and rinsing vegetables or fruit, as well as the cooking and packaging materials that will be used. Some commercial baby foods have been criticized for their contents.

This communication is focused on the determination of organophosphorus pesticides (OPs) and phthalates (PAEs) by means of a method based on ultrasound-vortex-assisted liquid-liquid microextraction coupled with GC-IT/MS (UVALLME-GC-IT/MS). The developed protocol allows the determination of six PAEs (1 DMP, 2 DEP, 3 DBP, 4 iBcEP, 5 BBP, 6 DEHP; below the GC-MS chromatogram of a turkey sample is reported) and 16 OPs. 0.1 g of freeze-dried product sample are dissolved in 10 mL of warm distilled water along with 2 μL of Internal Standard (anthracene 10 mg mL^{-1} in acetone): the choice of extraction solvent is studied starting from the n-heptane, just used for PAE determination in similar matrixes. The solution, held for 5 minutes on the vortex mixer and for 6 min in an ultrasonic bath to 100 W for favoring the solvent dispersion and consequently the analyte extraction, is centrifuged at 4000 rpm for 30 minutes: 1 μL is injected into the GC-IT/MS (capillary column SE54: 30 m, ID 0.25 μm, d 0.25 mm). All the analytical parameters investigated will be deeply discussed. The method has been applied to real commercial freeze-dried samples: the results do not show significant contaminant values.



Calibration of Commercial and Modified Polar Organic Chemical Integrative Samplers (POCIS) for the Analysis of Emerging Pollutants in Waters

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Human health and ecosystems are threatened by the release and the accumulation of emerging pollutants in the aquatic environment, which needs to be constantly monitored. For this reason, many recent studies are focused on the analysis of compounds used in everyday life, like pharmaceuticals or personal care products. These substances are not entirely absorbed by human body, reaching the aquatic compartment mainly from wastewater treatment plants and effluents from hospitals and pharmaceutical production facilities[1]. The main analytical problems related to the determination of these compounds are represented by their very low concentration levels (ng/L or below) and the presence of potential interferents[2]. Therefore, the combination of passive sampling and LC-MS/MS represents an alternative and powerful approach to successfully reach the goal of their analytical determination.

Our group has developed a method for the determination of nonsteroidal anti-inflammatory drugs in drinking water by passive sampling[3], in particular using the Polar Organic Chemical Integrative Samplers (POCIS)[4]. Analyte concentration measured in the POCIS sampler can provide Time-Weighted Average concentration of contaminants in water if the sampling rate of each specific compound is known; a simple calibration system has been developed to this aim[5]. More recently, the method has been extended to other compounds which are representative of various classes of emerging pollutants: pharmaceuticals (ibuprofen, naproxen, diclofenac, ketoprofen, mefenamic acid, gemfibrozil, carbamazepine), perfluorinated compounds (PFOA, PFOS), triclosan (an antimicrobial agent used in many personal care products) and caffeine (a potential chemical marker of human contamination). Analyses were carried out on an Agilent 1200 SL Liquid Chromatograph
with Zorbax XDB-C18 column, coupled to an Agilent 6430 Triple Quadrupole equipped with ESI interface; quantitation was achieved by multiple reaction monitoring mode to maximize sensitivity, using the internal standard method with isotopically labelled compounds.

The effect of different environmental condition (i.e. water flow and temperature) on the POCIS calibration has been studied. Besides, a new configuration of the sampler, which differs from the commercial one for the membrane porosity has been studied; the first results are really interesting, highlighting a significant enhancement in the sampling rate for many analytes. If this will be confirmed it should be possible to reduce the deployment time of the POCIS, extending the applications of this passive sampler.

Examples of monitoring studies investigating the presence of these emerging pollutants in drinking water treatment plants of Northern Italy will be presented.

References

1. Tanwar S., Di Carro M., Ianni C., Magi E.; in: “Personal Care Products in the Aquatic Environment”, Berlin, Heidelberg, 2015, 37-71, M.S. Diaz-Cruz and D. Barcelo´ (Eds.).
2. Fatta-Kassinos D., Meric S., Nikolaou A.; *Anal. Bioanal. Chem.*, 2011, *399*, 251-275.
3. Tanwar S., Di Carro M., Magi E.; *J. Pharmac. Biomed. Anal.*, 2015, *106*, 100-106.
4. Alvarez D.A., Petty J. D., et *al.*; *Environ. Toxicol. Chem.*, 2004. *23*, 1640–1648.
5. Di Carro M., Bono L., Magi E.; *Talanta*, 2014, *120*, 30-33.

A New Validated Gas Chromatographic-barrier Ionization Discharge Detector (GC-BID) Method for the Monitoring of CO_2 and N_2O Emissions from Settling and Disinfection Units in Wastewater Treatment Plants (WWTPs)

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The reduction of greenhouse gas (GHG) emissions is nowadays a well-defined path at European level far beyond the fateful 20-20-20 agreed in Kyoto in order to achieve a climate change mitigation (https://ec.europa.eu/clima/policies/strategies/2050_en). In this respect, the monitoring of GHG emissions from wastewater treatment plants (WWTPs) is of increasing interest, to improve the knowledge about biological processes and operational conditions in WWTPs for lowering the environmental impact[1]. However, standard procedures are not available yet, so there is a need for analytical methods to identify and quantify these gases (i.e. CO_2 and N_2O). To our knowledge, even though a broad spectrum of detectors, chromatographic columns and operating conditions have been proposed for analyses of CO_2 and N_2O, few studies dealing with their simultaneous analysis are actually available in the scientific literature[2]. In this communication, we describe the development and the validation of a method based on gas chromatography (GC) equipped with a barrier ionization discharge (BID) detector, allowing us the simultaneous high-precision measurements of N_2O and CO_2 emissions. For CO_2 and N_2O it was possible to validate the method with relative standard deviations (RSD%) less than 6.6% and 5.1%, respectively, in agreement with the ICH acceptance criteria for precision[3]. In order to support the method's accuracy, gas standard mixtures containing mixed certified concentrations of CO_2 (542 and 730 ppm_v) and N_2O (400 and 602 ppb_v) were used as reference materials. A good linearity was achieved, with a determination coefficient (R^2) not lower than 0.998, within concentration ranges of 50-1000 ppm_v and 250-50000 ppb_v for CO_2 and N_2O, respectively. The limit of detection (LoD) was 62.0 ppb_v for N_2O and 5.3 ppm_v for CO_2; the limit of quantification (LoQ) was 188.0 ppb_v for N_2O and 16.0 ppm_v for CO_2 [4]. The validated GC-BID method was successfully applied for analysis of N_2O and CO_2 emissions from full-scale WWTP located in Potenza (Basilicata, southern Italy), focusing the attention on not-areated units (i.e., secondary settling and disinfection unit) poorly investigated[5]. The obtained results suggested that the validated GC-BID method could contribute to the further development of a standard methodology for GHGs measurement, which is actually not available. Moreover, innovative configurations of WWTPs could be proposed for settlers in order to reduce the wind effects on GHG emissions, mostly in windy areas and the alternative oxidants could be used as disinfection agents.

References

1. Caivano M., Bellandi G., Mancini I.M., Masi S., Brienza R., Panariello S., Gori R. and Caniani D.; "Monitoring the aeration efficiency and carbon footprint of a medium-sized WWTP: experimental results on oxidation tank and aerobic digester", *Environ. Technol.*, 2016, *11* (6), 1-10.
2. Hedley, C.B., Saggar, S., and Tate, K.R., "Procedure for fast simultaneous analysis of the greenhouse gases: methane, carbon dioxide, and nitrous oxide in air samples"; *Communications in Soil Science and Plant Analysis*, 2006, *37* (11-12), 1501-1510.
3. Swartz M.E., Krull I.S.; *Handbook of Analytical Validation*, CRC Press, NewYork, 2012.
4. Pascale, R., Caivano, M., Buchicchio, A., Mancini, I. M., Bianco, G. and Caniani, D., "Validation of an analytical method for simultaneous high-precision measurements of greenhouse gas emissions from wastewater treatment plants using a gas chromatography-barrier discharge detector system"; *J. of Chromatography A*, 2017, *1480*, 62-69.
5. Redmon D., Boyle W.C. and Ewing L., "Oxygen transfer efficiency measurements in mixed liquor using off-gas techniques"; *Water Pollut. Control Fed.*, 1983, *55* (11), 1338–1347.

Development of a Prototype Analytical Apparatus for the Quantitative Determination of the Composition of Fluids in Synthetic Rocks.

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The quantitative assessment of fluids' composition arising from rocks formation processes is crucial in modeling geological processes. The relative concentrations of the so called "COH fluids" (namely, H_2O, CO_2, CH_4, CO, H_2, O_2, together with N_2) can drive the formation process to completely different directions: as an example, the H_2O/CO_2 ratio, can influence the melting temperatures, the location of hydration or carbonation reactions, and the solute transport capability in several rock systems. In the scientific literature, COH fluids speciation has been generally assumed on the basis of thermodynamic calculations using equations of state of simple H_2O–nonpolar gas systems (e.g., H_2O–CO_2–CH_4). The limit of this approach relies on the fact that the behavior of more complex systems is predicted in a rough way. An apparatus which is able to perform the quantitative determination of COH fluids in experimental rocks synthesis is then needed to study such complex systems in a proper way.

From an analytical point of view, this is a quite intriguing challenge because, as very high pressures ($P > 1GPa$) are employed, only few milligrams of rock can be prepared, with fluids representing about 10^{-3}-10^{-4} of the initial rock weight. Moreover, high accuracy and precision are requested for such determinations, making even more difficult the development of proper instrument.

In this contribution, we present a new developed apparatus for the analysis of COH fluids in capsules deriving from rocks synthesis experiments, which allows the quantitative determination of volatiles in the fluid by means of a home-made capsule-piercing device connected to a quadrupole mass spectrometer. This strategy allows the analysis of all the gases delivered from rocks, and not only of a part of them, leading to the high sensibilities required to reach the targeted issues.

A quantitative analysis of COH fluids along with associated statistical errors is obtained by matrix linear regression of the m/z data of the sample and of standard gas mixtures of known composition.

Confirmatory experiments on well-known systems were conducted to verify the absence of bias.

The estimated uncertainties fulfill the initial requests as they are typically <1% for H_2O and CO_2, and <5% for CO. Preliminary results one some interesting systems will be also presented.

Solid-phase Extraction of Trace Glucocorticoids from Environmental Waters on Silica-supported Humic Acids-derived Carbons Followed by HPLC-ESI-MS

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Being widely employed both in human and veterinary medicine, largely excreted with no structural modification, and not quantitatively abated by wastewater treatment plants, GCs are major emerging pollutants and their environmental widespread is reason of great concern due to their persistence and adverse effects, mainly endocrine disruption[1]. The typical concentrations levels detectable in environmental waters almost range from few to some hundred nanograms per litre[1,2], thus requiring a pre-concentration step before instrumental analysis. In this work, micrometric silica was modified with a carbonaceous phase obtained by thermally treated commercial HAs (600°C, N_2 flow, 1 h), previously physisorbed on the inorganic support. The obtained material (10 wt% HA@silica) was tested as a novel carbon-based sorbent for SPE of eight glucocorticoids (GCs) from environmental waters. Pre-concentration tests were undertaken on tap water samples (50 mL) enriched with 0.5-5 µg/L of each GC (prednisolone, prednisone, hydrocortisone, cortisone, betamethasone, dexamethasone, triamcinolone acetonide, fluocinoloneacetonide acetate), using 200 mg of sorbent packed in 3 mL SPE tubes (flow rate ~ 5 mL/min). Quantitative adsorption was observed at the sample native pH for all the analytes, which were simultaneously eluted in a single fraction (2.5 mL methanol) gaining quantitative recovery (90-110%, *n*=3). The HA@silica cartridge proved to be reusable for at least three pre-concentrations, with unchanged performance. The SPE procedure was also tested in raw river water samples, fortified with the target compounds at concentration levels in the range 50-500 ng/L, providing good recovery (70-112%, *n*=3) and enrichment factors (e.f.) up to 200. The lowest concentration detectable can be further improved with e.f. up to 2000 by evaporation of the eluate under N_2 stream. After SPE, GCs were separated and quantified by HPLC-ESI-MS/MS, obtaining good linearity in the range 10-100 µg/L, and specific detection (MRM mode). Further tests are ongoing on seawater and wastewater treatment plant effluents in order to investigate the applicability of the proposed SPE material to various/complex environmental matrices. A full characterization of HA@silica, including scanning electron microscopy, thermogravimetric analysis, Fourier transform infrared spectroscopy, BET surface area measurements, X-ray photoelectron spectroscopy, is now in progress. The main figures of merit, that is selectivity, sensitivity, linearity, recovery, precision and batch-to-batch reproducibility will be evaluated, and the final analytical method will be applied to the analysis of actual-world water samples. In view of the good performance of HA@silica, this material could be tested also for pre-concentration of other classes of emerging pollutants.

References
1. *J. Chromatogr. A*, 2012, 1224, 19-26.
2. *Chemosphere78*, 2010, 972-979.

Aliphatic Amines in Atmospheric Aerosol: Sources and Distribution

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Amines are atmospherically-relevant organic compounds, contributing to new particle formation[1] and to the production of toxic species[2]. They are mainly present in the gaseous phase, but they are partially converted into particulate phase after neutralization. The most common and abundant amines observed in particulate matter are aliphatic low-molecular-weight amines[2,3]. More than one hundred of different molecules belong to this class, the most abundant of which are Ethyl-amine (EA), Methyl-amine (MA), Diethyl-amine (DEA), Trimethyl-amine (TMA) and Dimethyl-amine (DMA). Till now different sources have been identified, which are mainly located in rural areas, such as animal husbandry, agricultural activities, biomass burning. Other minor sources are expected to be treatment of sewage and waste, combustion, industry, automobiles, cooking, tobacco smokes, composting operations and natural sources such as oceans, biodegradation of organic matter (that contains amino acids) and geologic sources[3]. The class of methyl amines is the most common in the atmosphere and has the highest concentrations near major sources, with a total global emission of 285 Gg N year^{-1}. TMA, the prevalent amine in the atmosphere, is estimated to have a global flux at approximately 170 Gg N year^{-1}, which is the highest among all alkylamines. It's believed that most of this flux comes from animal husbandry activities[3,4]. This study analyzes the spatial and seasonal variation of aliphatic amines in one of the european areas characterize by high nitrogen emissions[5]. Pm$_{10}$ samples were collected in northern Italy in one urban site in Milan and in two rural sites in the southern part of Lombardy (corte dei cortesi - cdc and schivenoglia), characterized by intense agricultural and zootechnical activities. Nitrogen organic species were first investigated by Fourier-transform infrared spectrometry. Then, aliphatic amines were quantified by ion chromatography (IC)[6]. After the set-up of the methodology, chromatography separation was achieved using a methanesulfonic acid (MSA) gradient elution on a dionex cs17 column with conductivity suppressor (dionex cprs 500), which has allowed the quantification of the main cations as well. The analytical results show higher concentration in the rural sites than at the urban one. Concentration of single amine compounds can be as high as 100 ng m^{-3}. The correlation of MA with K^+ and levoglucosan, tracers of biomass burning, suggests that one of the most important sources for this amine is residential heating. In the rural site, an increase in the DMA concentration has been observed (up to 36 ng m^{-3}) in early summer, likely due to the use of pesticides (indeed DMA is a component of pesticides). Amines can potentially be significant markers to track the impact of agricultural emissions and wood burning on air quality.

References
1. Kulmala, et *al.*, "Direct observations of atmospheric aerosol nucleation"; *Science*, 2013, *339*, 943–946.
2. Healy, R. M., Evans, G. J., Murphy, M., Sierau, B., Arndt, J., McGillicuddy E., O'Connor, I. P., Sodeau J. R., Wenger J. C.; *Anal. Bioanal. Chem.*, 2015, *407*, 5899-5909.
3. Ge, X., Wexler, A.S., Clegg, S.L.; *Atmos. Environ.*, 2011, *45*, 524-546.
4. Schade, G.W., Crutzen, P.J., J.; *Atmos. Chem.*, 1995, *22*, 319-346.
5. M.A. Sutton, C.M. Howard, J.W. Erisman, G. Billen, A. Bleeker, P. Grennfelt, H. van Grinsven, B. Grizzetti; "The European Nitrogen Assessment: Sources, Effects and Policy Perspectives"; 2011.
6. VandenBoer, T. C., Markovic, M. Z., Petroff, A., Czar, M. F., Borduas, N., and Murphy, J. G.; *J. Chromatogr. A*, 2012, *1252*, 74-83.

Elemental and Organic Carbon contribution to atmospheric aerosol at Ny Ålesund (Svalbard Islands)

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Substantial climatic changes are affecting the Arctic since the past decades and, in this context, the atmospheric aerosol plays a key role in the current climatic changes, influencing the energy budget of the surface and lowermost atmosphere. In particular, during polar sunrise, the Arctic troposphere is a unique chemical reactor, due to emissions both from human activity in the mid/high latitude areas and from natural sources in the Arctic Ocean.

Moreover, light-induced chemical reactions are able to cause changes in atmospheric composition. The coupled effect of meteorological patterns and extreme variations in solar irradiance starting in spring makes difficult to unravel the factors of the production and removal of many environmentally relevant chemical compounds.

At this purpose, daily PM10 and size-segregated (by 4-stage impactor) aerosol samples were continuously collected at Gruvebadet station (Ny Ålesund, Svalbard Islands, 78.9°N, 11.9°E) during the spring-summer period (March-September) along six consecutive years (2010-2015) and were analysed for ion, metal and EC/OC (Elemental/Organic carbon) content.

Here we focus on the EC and OC fraction of the aerosol and on selected organic anions (oxalate, acetate, propionate, formate, glycolate and pyruvate), because of their importance in the absorption of solar radiation (EC) and their sensitivity to oxidation processes and to the dynamic atmospheric production/consumption triggered and/or mediated by solar radiation (OC and organic compounds). Most of the determined organic anions show very low concentration in all the years, with the exception of oxalate, which is always dominant among the organic anions.

The temporal trends of the measured compounds is studied in comparison both with the broad band UV solar irradiance data in order to evaluate the effect of the photochemistry on the studied compounds.

Moreover, correlations among different chemical markers are studied, together with backtrajectory analysis, in order to highlight the long-range transport events delivering these compounds together with pollutants from the anthropised areas of the Northern hemisphere. For instance, in particular periods, significant correlation between nitrate and organic acids are found, whose nature is still to be ascertained and which could be related to common photochemical production processes. Besides, the similarity in the spring pattern of sulphate and oxalate hints at a common anthropogenic source of the latter in this period and requires further investigation.

Co-localization of DNA-based conformational switches for Single-Step Fluorescence Detection of Antibodies

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Antibody detection is crucial for the diagnosis of many human disorders including infectious, autoimmune, and oncological diseases[1]. Moreover, since immunotherapy represents nowadays the frontier to fight certain diseases, the detection of specific antibody becomes of paramount importance to correctly monitor the progression and efficacy of such therapies. To allow early diagnosis, prompt therapeutic actions and efficient immune-based therapy monitoring antibodies detection methods should be sensitive, quantitative and specific but also rapid and easy to use[2]. Unfortunately, however, current methods routinely used for this purpose in clinical settings either require reagent-intensive laboratory-based techniques (ELISA and other heterogeneous, sandwich-type assays), multiple time-consuming incubation steps (e.g. Western Blot assay, radioimmunoassay), and/or sophisticated equipment (e.g. surface plasmon resonance).

In an attempt to find new solutions to this problem here we propose a novel approach for the rapid, sensitive and single-step detection of antibodies that couple the advantageous features of DNA-based conformational switching probes with those of co-localization based approaches. Specifically, we take advantage of the spatial geometry, that is shared by all IgG and IgE antibodies (i.e. the majority of diagnostically relevant antibodies) to co-localize on the same antibody DNA-based elements that are rationally designed to give a measurable fluorescence signal only in the presence of a specific target antibody. We also demonstrated the possibility of multiplex detection of antibodies in the same solution using different sets of DNA-based elements. In an attempt to find the best practical application for our platform we have also demonstrated the ability on the use of this strategy for the monitoring of the immune response of patients that are under vaccine treatment.

References
1. Cutts, J. C., Powell, R., Agius, P. A., Beeson, J. G., Simpson, J. A., Fowkes, F. J.; *BMC Med.*, 2014, *12*, 150.
2. Gubala V, Harris L.F., Ricco A.J., Tan M.X., Williams D.E.; "Point of care diagnostics: status and future"; *Anal. Chem.*, 2012, *84*, 487.

Colloidal Nanoparticle modified Graphene-based electrochemical platforms for clinical biomarker detection

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Nowadays, graphene-modified electrodes and their application to electrochemical sensing have attracted enormous interest. The main advantages of graphene-based electrodes are a large potential window, fast heterogeneous electron transfer kinetics for various analytes and the involvement of additional "chemical features" (e.g. aromatic structures strongly connecting graphene via π−π stacking interactions). The integration of Au nanoparticles (NPs) into graphene nanoflakes allows in certain cases to efficient improvement of the device sensitivity due to enhancement of the electron transfer or through its surface catalytic reaction with certain analytes (e.g. hydrogen peroxide). DNA sensing is another application of Au NP/graphene hybrids. The behavior of a novel AuNPs-graphene nanostructure was, herein, investigated towards electrochemical sensing of human metabolites[1] and towards the development of a DNA-based biosensor (genosensor). In particular, the novel electrochemical platform was evaluated for the development of a genosensor for the detection of miRNAs, a family of small, non-coding RNAs that are considered important clinical biomarker candidates for many diseases, including cancer[2]. Electrochemical techniques, such as Electrochemical Impedance Spectroscopy (EIS), Scanning Electrochemistry Microscopy (SECM) and Differential Pulse Voltammetry (DPV), were used for the development and the characterization of the biosensing platform. In a first attempt, the DNA capture probes were immobilized onto the electrode surfaces. Afterwards, the target biotinylated RNA was hybridized with the specific capture probes. The biosensing platform was then incubated with a streptavidin-enzyme-conjugate and exposed to a proper substrate. The product of the enzymatic reaction was electrochemically monitored by DPV. In a further approach, EIS was used to develop a label-free method.

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References

1. C. Ingrosso et *al.*, *J. Mater. Chem. A*, 2017; doi: 10.1039/c7ta01425b.
2. D. Voccia et *al.*, *Biosensors and Bioelectronics*, 2017, *87*, 1012-1019.

Smartphone–based enzymatic biosensor for rapid detection of oxidase substrates using confined multilayer paper reflectometry

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The development of smartphone–based biosensors for point-of-care testing (POCT) applications allows realizing "all in one" instruments, with large potential distribution among the general population[1]. The advance in complementary metal oxide semiconductor (CMOS) camera technology makes the smartphone suitable as a detector for reflectance measurements that is the most popular, simple, inexpensive and straightforward method to detect paper color-based assays[2]. Despite the increasing interest of recent years in the development of color change paper-based biosensors, they still suffer from a poor detectability and reproducibility related to inhomogeneity of color development, which leads to a poor quantitative analysis performance. This issue can be attributed to the mobility of enzymes and reagents towards the edge of detection zone when the sample is applied onto paper surface. To overcome these problems, we propose a smartphone paper-based biosensor, in which all the reagents necessary to complete the analysis are co-entrapped on paper in a "wafer"-like bilayer film of polyelectrolytes (Poly (allyl amine hydrochloride/poly (sodium 4-styrene sulfonate))[3]. The sequential adsorption of oppositely charged polyelectrolytes by layer-by-layer (LbL) deposition technique was exploited to obtain self-assembled polyelectrolyte multilayer thin films. The main advantages of this method are the possibility to control the structure and the total film thickness on a molecular level and the efficient selective entrapment of biomolecules such as enzymes exploiting non-covalent bonding and preserving biological activity in their microenvironment. The smartphone-based device was realized using a 3D printing low-cost technology. Its components are a semi-cover accessory attached to the smartphone, a polydimethylsiloxane (PDMS) light diffuser placed in front of the smartphone flash LED to improve the image quality, a mini dark box and a disposable analytical cartridge containing the bioactive paper-based support necessary for the analysis. The biosensor was developed exploiting coupled enzyme reactions for quantifying oxidase substrates such as L-lactate in oral fluid, which is considered a biomarker of poor tissue perfusion in sports performance evaluation. The developed method is sensitive, rapid and it allows detecting L-lactate in the relevant physiological range, with a limit of detection of 0.1 mmol L^{-1}. The extreme simplicity of assay execution (no reagents need to be added) together with the high versatility (the assay is HRP-based color change detection of H_2O_2 produced by an analyte-specific oxidase), make our approach generally applied for all oxidases, thus enabling the development of other specific bioassays to quantify several biomarkers such as glucose, cholesterol, ethanol, cortisol, xanthine and bilirubin.

References
1. Roda, A. et *al.*; *Analytical Chemistry*, 2014, *86* (15), 7299-7304.
2. Hu, J. et *al.*; *Biosensors and Bioelectronics*, 2014, *54*, 585-597.
3. Calabria, D. et *al.*; *Biosensors and Bioelectronics*, 2017, *94*, 124-130.

A Reagentless Paper-based Screen-printed Device to Detect Chloride Ions in Serum and Sweat

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Screen-printed electrodes (SPEs) are the ideal device to detect a plethora of species, but they often require additional tasks by the operator and their disposal is not always "green". We report a novel paper-based SPE for the detection of chloride in biological samples. With an easy manufacturing methodology, we developed a one shot and reagent-free electrochemical platform to selectively detect chloride ions in serum and sweat. To this purpose, a silver-based three-electrode configuration is utilized. The detection mechanism is based on the oxidation of the Ag contained in the ink to Ag^+, which reacts with the chloride (Cl^-) present in the sample. The formed silver chloride (AgCl) is successively reduced at the working electrode and these processes produce an oxidation and a reduction wave in the cyclic voltammogram curve, used to quantify the level of Cl^-. Chloride has been detected linearly up to 200 mM with a detection limit equal to 1 mM and a repeatability lower than 10%. The accuracy of the sensor has been evaluated in serum and sweat samples, achieving recovery values ranging from 93 ± 10 % and 108 ± 8 %. Moreover, the analysis of five serum samples provided by the Hospital gave comparable results with respect to the gold standard method (Ion Selective Electrode) adopted in routine clinical analyses, demonstrating the suitability of this paper-based device.

PVA/GO/Au: Development and Characterization of a New Electrode Material

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In the last years the use of nanostructuring materials has increasingly spread in many scientific and applied technologies fields. Chemically modified electrodes (CMEs) can be made using nanomaterials, organic monolayers or composite hybrid system developed by fusion of organic polymers and nanostructured electroactive species. These different strategies for modifying electrodes provide opportunities to confer a unique range of properties to electrode surfaces, like an improvement of electrode surface areas or electrocatalytic behavior, obtaining electrodes with useful switchable properties[1]. Nanomaterials are often made by carbon nanostructures or metallic nanoparticles not only as pure metal but also as alloys and/or oxihydroxide forms. Carbon nanostructures, like graphene, graphene oxide, and nanotubes, are widely used because of their interesting properties such as large specific surface area, high thermal and electrical conductivities, great mechanical strength and low cost[2,3]. Many transition metals show interesting electrochemical properties in terms of conductibility, stability and catalytic activities. In this respect, Au species present important electrocatalytic performance toward the electrooxidation of various organic molecules in aqueous medium[4,5]. In this study, we develop a new CME using a composite active material based on graphene oxide dispersed within the polyvinyl alcohol (PVA) and doped with electrodeposited Au particles (PVA/GO/Au). The PVA, although is scarcely employed in electrochemical applications, represents a versatile and interesting polymer employed in many fields of applied technology, such as medicine[6], and anti-corrosion coating polymer[7].

The glassy carbon was modified by casting 10 μL GO/PVA emulsion on the surface electrode and successively, Au particles were electrodeposited using an optimized pulsed electrochemical procedure by buffer carbonate solutions (pH= 8) containing 5.5 mM $HAuCl_4$.

The PVA/GO/Au electrode was electrochemically characterized as electrocatalyst toward the electrooxidation of alditols and carbohydrates in alkaline medium. Scanning electron microscopy (SEM) and X-Ray photoelectron spectroscopy (XPS) were used in order to characterize the morphology and the chemical speciation of the electrode surface. In addition, the modified electrode was characterized as a capacitor system during continuous charge-discharge process in alkaline medium.

References

1. R. C. Alkire, D. M. Kolb, J. Lipkowski, P. N. Ross, "Chemically modified electrodes"; Wiley – VCH, 2009.
2. Y. Zhu, S. Murali, W Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, *Advanced Materials*, 2010, *35*, 3906-3924.
3. J. Kim, L. J. Cote, F. Kim, W. Yuan, K. R. Shull, J. Huan; *Journal of American Chemical Society*, 2010, *132*, 8180-8186.
4. Y. Hu, J. Jin, P. Wu, H. Zhang, C. Cai; *Electrochimica Acta*, 2010, *56*, 491-500.
5. L. D. Burke, D. T. Buckley, J. A. Morrissey; *Analyst*, 1994, *119*, 841-845.
6. G. Orlando; "Regenerative Medicine Applications in Organ Transplantation"; *Academic Press*, 2013.
7. NPCS Board of Consultants & Engineers, "Handbook on Textile Auxiliaries, Dye and Dye Intermediates Technology", Asia Pacific Business Press Inc., 2009.

Glucose/Oxygen Enzymatic Fuel Cell Based on a "Green" Gold Nanoparticles Modified Graphene Screen-Printed Electrode for Glucose Detection in Human Saliva

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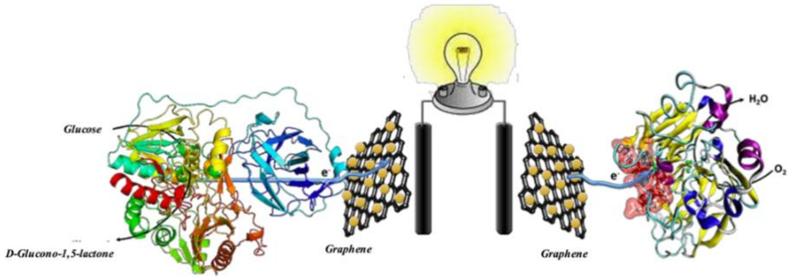
The aim of this work is to realize a miniaturized high-power glucose/oxygen enzymatic fuel cell (EFC) based on efficient DETs, employing cellobiose dehydrogenase (CDH) and laccase, respectively, and using a single screen-printed graphene electrode modified with "green" AuNPs. In fact, among the enzymes able to perform DET with the electrode surface, CDH is receiving great attention thanks to its ability to show DET upon reaction with many substrates including sugars, such as glucose and lactose[1,2].



The bioanode and biocathode are a graphene working electrode and a graphite counter electrode localized on the same screen printed electrode (SPE) modified with poly (vinyl alcohol) N-methyl-4(4'-formylstyryl) pyridinium methosulfate acetal (PVA-SbQ)/cellobiose dehydrogenase from *Corynascus thermophilus* (CtCDH) C291Y/AuNPs and with *Trametes hirsuta* laccase (ThLac)/AuNPs, respectively. In order to optimize the bioanode, several CDH immobilization procedures were adopted, such as drop-casting, use of Nafion membrane or PVA-SbQ photopolymer. The photopolymer showed the best performances due to its high internal flexibility allowing an easy re-orientation of the enzyme through the electrostatic interactions between enzyme and gold nanoparticles (AuNPs)[3]. Furthermore, the use of the nanomaterials allowed to reduce the overpotential of O_2/H_2O redox reaction catalyzed by *Trametes hirsuta* Laccase (ThLac), drop-casted onto the AuNPs modified SPE. The performances of bioanode and biocathode were tested separately, initially immobilizing both enzymes onto separated graphene SPEs. Successively, the bioanode and biocathode were assembled in a non-compartmentalized EFC and a remarkable 50% decrease of the maximum power output at the value of 2.15 ± 0.12 $\mu W\ cm^{-2}$ at cell voltage of 0.48 V and an OCV of 0.62 V at pH 6.5 was registered. In order to miniaturize the device, the bioanode and biocaythode were realized by immobilization of both enzymes onto the same SPE. The so miniaturized EFC delivered maximal power output of 1.57 ± 0.07 $\mu W\ cm^{-2}$ and 1.10 ± 0.12 $\mu W\ cm^{-2}$ with an OCV of 0.58 V and 0.41 V in a 100 μM glucose solution and in human saliva, respectively[4].

References
1. P. Bollella, F. Mazzei, G. Favero, G. Fusco, R. Ludwig, L. Gorton, R. Antiochia; *Biosens. Bioelectron*, 2017, *88*, 196-203.
2. R. Ortiz, M. Rahman, B. Zangrilli, C. Sygmund, P. O Micheelsen, M. Silow, M. D Toscano, R. Ludwig, L. Gorton; *Chem. Electro. Chem.*, 2017, *4*, 846-855.
3. P. Bollella, C. Schulz, G. Favero, F. Mazzei, R. Ludwig, L. Gorton, R. Antiochia; *Electroanalysis*, 2017, *29*, 77-86.
4. M. Falk, Z. Blum, S. Shleev; *Electrochim. Acta*, 2012, *82*, 191-202.

Generation IV Ionic Liquids and Nanomaterials to Develop Innovative Electrochemical Biosensing Platforms

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Different types of modified electrodes have been prepared and tested to assembly and construct portable sensing devices, useful to analyze, in a simple, fast and economic way, many analytes.

Bare glassy carbon electrodes (GCE) of the screen-printed type (SPE), with silver electrode as reference, have been modified, via drop casting on the working electrode surface, with a mixture of generation IV room temperature ionic liquids (RTILs) and nanomaterials.

The ionic liquids choline-amino acids, were synthetized in our laboratory following the methodology known in literature[1]. These RTILs differ from the previous generation ones because they are nontoxic and completely biodegradable[2,3]. Like those of the previous generations, the RTILs used in this work have interesting properties regarding low volatility, low flammability, high ionic conductivity, high chemical and electrochemical stability[4]. Furthermore, these compounds allow to significantly increase the work potential range (V), electroactive area (A_{ea}) and electron transfer constant (k_0), so that anode or cathode peaks can be detected even for extremely low concentration of analytes.

The nanomaterials used in this work were Multi-Walled Carbon Nanotubes (MWCNT) and Titanium Dioxide nanoparticles (anatase form). These two nanomaterials have been used both alone and together in different proportions with the chosen RTIL [Ch] [Phe]. All the so developed electrodes have been studied by means of cyclic voltammetry measurements to calculate the electroactive area (A_{ea}) of the working electrode, in order to find the best combination of nanomaterials/ionic liquid/water for the drop casting mixture.

All the proposed combinations have also been studied for stability: cyclic voltammetry measurements have been carried out at various time intervals after the preparation to investigate variations of the A_{ea} of the modified electrodes.

The electrochemical platform so developed has been used, after functionalization with the proper enzyme, as a biosensor. In particular, it has been tested for measuring glucose in food matrices and antioxidants in olive oils using Glucose Oxidase[5] and Lipase[6] respectively.

References

1. S. De Santis, G. Masci, F. Casciotta, et *al.*; *Phys. Chem.*, 2015, *17*, 20687.
2. J. Arning, S. Stolte, A. Böschen, F. Stock, W.R. Pitner et *al.*; *Green Chem.*, 2008, *10*, 47-58.
3. A. Romero, A. Santos, J. Tojo, A. Rodriguez; *J. Hazard Matter*, 2008, *151*, 268-273.
4. J.S. Xu, G.C. Zhao; *Int. J. Electrochem. Sci.*, 2008, *4*, 519-527.
5. M.L. Antonelli, F. Arduini et *al.*; *Biosensors and Bioelectronics*, 2009, *24*, 1382-88;
6. Álvarez G.A., J.A. Rodríguez, J.C. Escamilla, C.A. Galán; *J. Mex. Chem. Soc.*, 2015, *59*, 19-23.

Identification of bioactive peptides derived from cauliflower by-products by multidimensional liquid chromatography and bioinformatics

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Brassica crops, a huge vegetable family mainly constituted by cauliflower and broccoli, have a world production of about 22.3 million tons. Most of the production comes from Asia (with 82% of the total production), whereas Italy is the second world producer (with 0.4 million tons), followed by Spain and Mexico (http://faostat3.fao.org/). As a consequence of this intensive production, tons of cauliflower by-products are generated every year, and they are mainly made up of leaves (50% of the total) and stems. These residues might cause huge economic and environmental problems, and that is the reason why it is important to discover new uses of these waste materials, outside the agricultural sector as well, in order to create sustainable value chains in the farming and processing sectors[1].

At the same time the use of food industry-related by-products is also gaining interest, since it is now well known that some specific residues generated during food manufacture possess significant amounts of bioactive compounds. Correlated to Brassica crop, recent works have shown that cauliflower by-products are a good source of phenolic compounds, mainly flavonol derivatives[2]. While many studies reported the presence of AO and anticancer compounds in broccoli[3], the bioactive peptides (BAPs) remain poorly investigated.

The main objective of this study was the development of a new systematic analytical approach for the recovery, separation, identification of BAPs. In particular, in this study, we employed a platform based on two different extraction methods, comparing a sodium dodecyl sulphate (SDS) and ethylenediaminetetraacetic acid (EDTA) based protocols, followed by an in vitro digestion by two different enzymes, trypsin and a mixture of pancreatin and pepsin. The four protocols were tested for the ACE-inhibitory and AO activity. The protocols providing the highest bioactivity were purified by a combination of consecutive chromatographic separations, first by RP liquid chromatography and then by hydrophilic interaction chromatography (HILIC). The most active fractions, obtained from the second chromatographic dimension, were further analysed by nanoRP-HPLC coupled with an Orbitrap mass spectrometry for peptide sequencing. After database search, the identified peptides were further mined by in-silico analysis using PeptideRanker, which provided a bioactivity score later used to select candidates for chemical synthesis. Finally, on the basis on the probability as calculated by PeptideRanker algorithm and on the area, 6 peptides were selected and synthesized. The synthesized peptides were validated compared to the natural occurring ones checking their retention times and fragmentation patterns in cauliflower by-product hydrolysates. Finally, their activities were determined by in-vitro bioassays on the individual peptide standards.

References
1. M. Herrero et *al*.; "Plants, seaweeds, microalgae and food by-products as natural sources of functional ingredients obtained using pressurized liquid extraction and supercritical fluid extraction"; *Trends in Analytical Chemistry*, 2015, *71*, pp. 26–38.
2. R. Llorach et *al*.; "Valorization of cauliflower (Brassica oleracea L. var. botrytis) by-products as a source of antioxidant phenolics"; *Journal of Agricultural and Food Chemistry*, 2003, *51*, pp. 2181–2187.
3. F.W. Ávila et *al*.; "Assessment of the anticancer compounds Se-methylselenocysteine and glucosinolates in Se-biofortified broccoli (Brassica oleracea L. var. italica) sprouts and florets"; *Journal of Agricultural and Food Chemistry*, 2013, *61*, pp. 6216–6223.

Solid phase extraction of dibenzyl disulphide on a molecularly imprinted polymer

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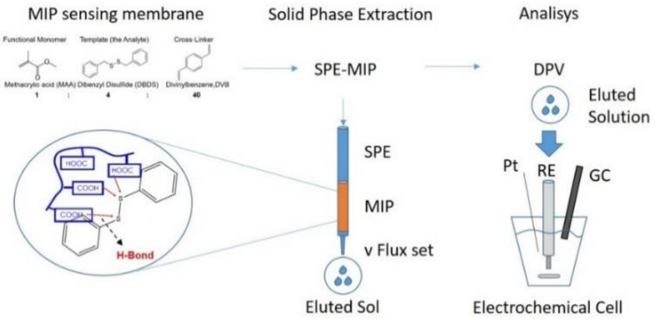
Dibenzyl disulphide (DBDS) is commonly present in power transformer oils as an antioxidant at concentration of around 100 ppm. Only recently it has been found to produce damages of these devices since it is corrosive for copper and cellulosic components[1]. It is possible, even if not easy, to control the composition of the oil in a transformer, so that the determination of DBDS in this particular matrix is of great interest for the prevention of the transformers failures. Many analytical methods have been proposed, based on chromatography with previous separation by liquid and solid phase extraction (SPE) with different sorbents[2]. Here a molecular imprinted polymer (MIP) is proposed for the first time for the selective extraction of DBDS from a power transformer oil. The procedure has been characterized by a new electrochemical method for the determination of DBDS in acetonitrile-ethanol (80:20) solution (DPV method), which has been purposely developed. This particular sorbent was considered because of its high selectivity which would allow an electrochemical determination without further separation. A scheme of the analytical procedure is reported below:



For the preliminary investigation, MIP was synthesized according to a previously described procedure[3], and then mechanically pulverized to particles of about 50 µm. DBDS was extracted from the polymer by repeated washing with ethanol and hexane. Successive extractions were controlled by UV, DPV, and EDS. MIP capacity in acetonitrile-ethanol (80:20) solvent at concentration of about 100 ppm is 2.4 10^{-3} mmol/gMIP, with a distribution coefficient K_D equal to 7. The adsorption of DBDS by column procedure was investigated by determining the breakthrough curve of a solution with 32 ppm of DBDS, on a column constituted by 0.2 g of pulverized MIP, and at elution rate of 0.2 ml/min[4]. The DBDS separation from a widely used transformer oil (Nytro Libra insulating oil from Nynas S.r.L. (Stockholm, Sweden) was successfully performed on the column described at the following conditions: 0.5 ml of oil introduced, 2 ml of acetonitrile-ethanol (80:20) solution for washing, 5 ml of acetonitrile-ethanol solution (80:20) for elution (110% recovery).

References
1. V. Dukhi, A. Bissesur, B. Martincigh; *Ind. Eng. Chem. Res*, 2016, *55*, 2911-2920.
2. I.E. Commisssion, in “Test methods for quantitative determination of corrosive sulfur compunds in unused and used insulating liquids”, 2012, IEC 62697-1.
3. N. Cennamo, L. De Maria, C. Chemelli, A. Profumo, L. Zeni, and M. Pesavento; *IEEE Sensors J.*, 2016, *16*, 7663-7670.
4. M. Pesavento, M. Sturini, G. D’Agostino, R. Biesuz; *Journal of Chromatography A*, 2010, 1217, 1208-1218.

Analytical Characterization of New Composites for Food Packaging Applications

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The application of metals and metal oxides in the form of nanostructured antimicrobials is continuously expanding. In the last decades, especially Cu- and Ag-based nanoantimicrobials [1] have attracted the interest of scientists and technologists, as assessed by the huge amount of reports on their synthesis and characterization [2]. Designing bioactive materials, with controlled metal ion release, exerting significant biological action and associated low toxicity for humans, is nowadays one of the most important challenges for our community. The most looked-for nanoantimicrobials are capable of releasing metal species with defined kinetic profiles, either slowing down or inhibiting bacterial growth and pathogenic microorganism diffusion [3]. In recent years, we have developed and deeply characterized many different nanoantimicrobial systems, ranging from Ag- and Cu-modified textiles [3] to bioactive food packaging [4]. On the one hand, all these materials were found to be human safe, since they showed no significant leaching of (potentially toxic) whole nanoparticles into contact media. On the other hand, antibacterial ionic species released by transition metal nanophases provided a powerful alternative route to fight bacterial resistance towards conventional antibiotics and disinfecting agents. Laser ablation synthesis in solution (LASiS), in particular, has been used in our labs to produce bioactive Cu- and Ag-based nanocolloids, both in aqueous and organic media, which can be used as water-insoluble nano-reservoirs in composite materials [5]. In fact, including nanophases into polymers (like polyethylene oxide or polylactic acid) allows to produce multifunctional packaging, combining biodegradable and antibacterial properties of both organic and inorganic phases. In this study, x-ray photoelectron spectroscopy was used to evaluate the chemical speciation and elemental composition of pristine nanoparticles and final materials, providing useful information about synthesis processes, as well as storage and processing conditions. Transmission electron microscopy was exploited to study morphologies of nano-colloids, along with UV-Vis and infrared spectroscopies for bulk chemical characterization. Electrothermal atomic absorption spectroscopy was used to investigate metal ion release from modified surfaces and industrial products. Analytical spectroscopy results were matched with bioactivity tests on target microorganisms of food spoilage. Different approaches to the synthesis and characterization of second-generation nanoantimicrobials, e.g. to those materials combining antibacterial efficiency and nanosafety issues, will be critically discussed, based on spectroscopic, morphological, release and bioactivity evidences.

References

1. M.D. Dizaj et *al*.; *Mat. Sci. Eng. C*, 2014, *44*, 278–284.
2. M.C. Sportelli et *al*.; *TrAC*, 2016, *84*, 131-138.
3. M.C. Sportelli et *al*.; Ch. n°8 in "Novel Antimicrobial Agents and Strategies", 2014, Wiley-VCH GmbH, 181-218.
4. M.C. Sportelli et *al*.; *Materials*, 2016, *9*, 544-557.
5. M.C. Sportelli et *al*.; *Nanomaterials*, 2016, *7*, 6-21.

Photocatalytic Transformation of C_2Cl_4 in Gas Phase Under UV-irradiated TiO_2

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The photocatalytic transformation of chlorinated solvents has been the topic of numerous works since the first studies of the photocatalytic processes under irradiated semiconductors. As an example, in the photocatalyzed transformation of perchloroethylene (PCE) in the presence of oxygen the $Cl^•$ radical has supposed to have a pivotal role in the first step of the degradation and in the successive transformation of the PCE by-products[1]. Also in aqueous solution, the role of halogen radicals was advanced to explain the formation of CCl_4 from chlorinated methanes[2].

In this work, we investigated the photodegradation of gaseous PCE on titanium dioxide films under UV light at 365 nm at the gas/solid interface. PCE conversion was carried out in a CSTR photo-reactor (Continuous Stirred Tank Reactor)[3] and the residual PCE leaving the reactor was properly detected using a PID detector and FTIR. The C_2Cl_4 photocatalytic transformation was investigated at different experimental conditions, such as at different PCE concentration, TiO_2 irradiated area, inlet gas flow and UV irradiance ($W{\cdot}m^{-2}$). The water vapor has a detrimental role on the PCE transformation rate due to the competition with PCE adsorption on reactive sites.

The rate and mechanism of transformation change when oxygen is present at high and negligible concentrations. Gaseous products of PCE degradation were determined: CO_2, phosgene, carbon tetrachloride (CCl_4), hexachloroethane (C_2Cl_6) and, at lower concentrations, trichloroacetyl chloride (TCAC) were identified as photodegradation products. In quasi-anoxic conditions, significant amount of adsorbed organic compounds with molecular weights higher than that of PCE were produced on the UV-irradiated TiO_2 surface and chloride ions are more accumulated at the surface, proof of the presence of a predominant reductive pathway. However, the addition of chloride ions on TiO_2 surface does not increase the production of gaseous CCl_4.

The production of active chlorine (sum of Cl_2, HClO and $ClO^•$) was investigated both in the presence of oxygen and in quasi-anoxic conditions. At low O_2 concentration no gaseous active chlorine was determined, while a significant amount was measured in the presence of oxygen. By considering that in the absence of O_2 the only possible form of active chlorine is Cl_2, the experimental evidences underline that the produced active chlorine is $HClO/ClO^•$. Then chlorine radical has a minor role in the abatement of C_2Cl_4.

These experimental data allowed us the identification of the main photodegradation pathways of PCE at high and low oxygen concentration giving intriguing and new insights into the photocatalytic transformation of chlorinated olefins from gaseous phase, putting the role of chloride radicals as reactive species back in a different perspective.

References
1. M. Nimlos, W. Jacoby, D. Blake, T. Milne; *Environ. Sci. Technol.*, 1993, *27*, 732.
2. C. Minero, A. Bedini, M. Minella; *Int. J. Chem. React. Eng.*, 2013, *11*, 717.
3. P. Calza, C. Minero, E. Pelizzetti; *J. Chem. Soc.*, 1997, *93* (21), 3765.

Microscopic and Spectroscopic Analysis with Synchrotron Light of Modified Surfaces of Technological Interest

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A fundamental aim of material sciences is to reckon the relationship between the properties of a device, and the morphological and structural characteristics of the surface. Combining basic electrochemical techniques with spectroscopic, microscopic and structural techniques is crucial for characterizing the structure-activity relationship for many different technological devices. We consider this approach even more interesting, if these electrochemical and structural characterizations are performed simultaneously under the control of the electrical potential. In this context during the last two decades, several interesting combined techniques emerged. In this talk we will present in-situ studies of electrochemical-spectroscopic, electrochemical-microscopic and electrochemical techniques combined with synchrotron radiation. In particular, technical EC-SPM (Electrochemical-Scanning Probe Microscopy) and EC-SRM (Electrochemical-Synchrotron Radiation methodologies) will be presented. We will present operando studies carried out employing these techniques to show the variation of the chemical, morphological and structural aspects of surfaces during straightforward electrochemical processes or by simply unplugging the electrical potential. The industrial impact, elicited by this experimental approach, will be also presented.

Metodi multi-block per l’analisi degli alimenti

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Analizzando dati chimici, qualora si abbia a disposizione un data-set con diversi blocchi di dati (usati come predittori in un modello di regressione o di classificazione), è stato dimostrato che sia più conveniente utilizzare degli approcci *multi-block* (detti anche di *data-fusion)*, ovvero dei metodi che permettano l’estrazione delle informazioni dai diversi blocchi di dati contemporaneamente, piuttosto che analizzarli individualmente (1). In chimica degli alimenti, accade sovente di avere dei data-set multi-block, principalmente perché gli stessi campioni possono essere analizzati con diverse tecniche analitiche. Numerose applicazioni di metodologie di *data-fusion* sono state effettuate in ambito alimentare; nel presente lavoro, particolare interesse verrà rivolto verso l’autenticazione e la classificazione di una birra artigianale prodotta nel Lazio (Birra del Borgo, Borgorose (RI)). I campioni sono stati analizzati mediante cinque differenti tecniche analitiche: Spettroscopia MIR, Spettroscopia NIR, Spettroscopia UV, Spettroscopia Visibile e termogravimetria. Le matrici di dati sono state utilizzate sia individualmente che congiuntamente al fine di realizzare i differenti modelli di classificazione (2). Per la creazione dei modelli con i blocchi individuali si è utilizzato PLS-DA (3), mentre per l’analisi multi-block dei dati sono stati utilizzati gli approcci Low- e Mid-Level data fusion (4) e Sequential and Orthogonalized-PLS (SO-PLS) combinati con la Linear Discriminant Analysis (LDA) (6-8). I risultati così ottenuti sono stati studiati sia dal punto di vista predittivo che dal punto di vista dell’interpretazione. In generale, tutti i metodi multi-block hanno fornito predizioni soddisfacenti, migliori dei risultati ottenuti mediante classificazione sui blocchi individuali; in particolare, il Mid-Level data fusion ha permesso di ottenere il 100% di corretta classificazione per tutti i campioni di test (una rappresentazione grafica dei risultati ottenuti mediante questo metodo classificativo è riportato in Figura 1). Dal punto di vista interpretativo, i modelli basati sul metodo SO-PLS hanno mostrato degli evidenti vantaggi.

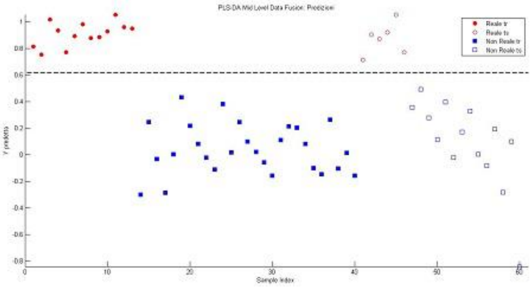

Figura 2: Predizioni Modello PLS-DA Mid Level Data Fusion

References

1. I. E. Frank and B. R. Kowalski; “Prediction of wine quality and geographic origin from chemical measurements by Partial Least-Squares regression modeling”; *Anal. Chim. Acta*, 1984, *162*, 241-251.
2. A. Biancolillo, R. Bucci, A. L. Magrì, A. D. Magrì, F. Marini; “Data-fusion for multiplatform characterization of an Italian craft beer aimed at its authentication”, *Analyt. Chim. Acta*, 2014, *820*, 23-31.
3. M. Barker, W. Rayens; “Partial least squares for discrimination”; *J. Chemometr.*, 2003, *17*, 166-173.
4. M. Bevilacqua, R. Bucci, A.D. Magrì, A.L. Magrì, F. Marini; “Data fusion for food authentication. Combining near and mid infrared to trace the origin of extra virgin olive oils”; *NIR News*, 2013, *24* (2), 12-15.
5. T. Næs, O. Tomic, B.-H. Mevik, H. Martens; “Path modelling by sequential PLS regression”; *J. Chemometr.*, 2011, *25*, 28-40.
6. R.A. Fisher; “The use of multiple measurements in taxonomic problems”; *Ann. Eugen.*, 1936, *7*, 179-188.
7. U.G. Indahl, H. Martens, T. Naes; “From dummy regression to prior probabilities in PLS-DA”; *J. Chemometr.*, 2007, *21*, 529-536.
8. A. Biancolillo, I. Måge, T. Næs; “Combining SO-PLS and linear discriminant analysis for multi-block classification”, *Chemom. Intell. Lab. Syst.*, 2015, *141*, 58-67.

An Innovative NIR Hyperspectral Imaging Approach to Pattern Cheese Ripening

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Biochemistry of cheese ripening is considered under two general headings: proteolysis and lipolysis. Proteolysis is the most complex biochemical activity that contributes to cheese ripening and flavour development through the formation of peptides and AA and by changing the texture of cheese from the breakdown of the protein network. Lipolysis in cheese is due to the presence of lipolytic enzymes that cleave the ester linkage between a fatty acid and the glycerol moiety of a triacylglycerol; it produces free fatty acids (FFA) with chain lengths ≥C4, glycerol, and mono- and diacylglycerols.
Several analytical methods are available to evaluate cheese ripening ranging from qualitative approaches, aimed at following process evolution, to quantitative approaches, which allow to quantify compounds being formed. In this work two reference methods were applied on several sub-samples radially located within cheese specimens to evaluate the degree of protein hydrolysis (DH) and the total free fatty acid (FFA) content – o-phthaldialdehyde (OPA) spectrophotometric assay and copper soap method, respectively. However, no technique was proposed yet to pattern cheese ripening, which is clearly influenced by location within a cheese and tends to evolve following a radial pathway from the centre to the borders of the cheese. Until now, a suitable sampling scheme has been the only prospective to account for such differences.
The aim of this work was the reliability evaluation of near infrared hyperspectral imaging (1000–2500 nm), to monitor not only the evolution but also the spatial extent of proteolysis and lipolysis in cheese. First of all, a qualitative assessment of the NIR bands associated with peptides and free fatty acids was carried out on a wide set of cheese, characterized by different ripening types: mainly proteolytic or mainly lipolytic. Then, a semisolid slicing cheese was followed during the early stages of its ripening, acquiring hyperspectral images daily for a total of 10 days from cheese production (three samples each day).
After the deploying of suitable pre-processing methods for minimising the amount of useless information within hyperspectral data, multivariate pattern recognition, both exploratory and supervised, allowed to efficiently map ripening across sample surfaces. In particular, principal component analysis (PCA), integrated with a brushing approach between score images and score plots, allowed to efficiently monitor cheese evolution and to characterise the different stages according to definite NIR absorption bands.
The results indicate that the NIR-HSI approach adds spatial information in cheese biochemical knowledges allowing to deeply understand the phenomena that occurs during cheese ripening.

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Development of a method for the quality control of polystyrene (EPS) based on the use of microscopy techniques and multivariate statistical methods

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Synthered Expanded Polystyrene (EPS) is a widely-used polymer both for packaging and for the production of handworks, as containers, surfboards etc. According to the final application, the handwork itself must exhibit mechanical properties that make it suitable for the final purpose. The industrial quality control of EPS products for different applications is usually carried out by mechanical methods and technological measurements.

In this work, an alternative method has been developed for the industrial quality control of EPS products, based on the surface characterization of the object by microscopy coupled to multivariate statistics. The method has been applied to samples either classified by classical quality control methods as suitable (OK) or not suitable (KO) for the final application purpose.

In particular, the samples belonged to different production lots of surfboards and containers; for each type of product, OK and KO samples were available.

The surface of the samples was characterized by recording images through optical microscopy with different acquisition settings. The Zernike's mathematical moments were then calculated for each image to obtain global descriptors of the image features. The set of mathematical indexes thus calculated was therefore used to build multivariate classification models for a future application in industrial quality control. To this purpose different classification methods were compared (PLS-DA, SIMCA, LDA etc), also coupled to variable selection strategies. The applied method proved to be a valid alternative to classical quality control, allowing at the same time an easy automation of the overall procedure.

Application of an electro-activated glassy carbon electrode (GCE) to the analytical monitoring and photochemical studying of acetaminophen

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The occurrence of emerging contaminants in surface waters, such as pharmaceuticals and personal-care products, is an environmental issue of high concern due to the toxic effects on ecosystems and humans[1]. *Waste Water Treatment Plants* (WWTPs) are usually not able to remove these compounds from wastewater because they are water soluble and biorefractory. Therefore, emerging contaminants are often released in water bodies. As far as pharmaceuticals are concerned, antibiotics, analgesics and anticonvulsionants are usually detected in surface waters[2]. In these environments, xenobiotics can undergo both abiotic and biotic degradation. Among abiotic pathways, direct and indirect photochemical reactions can be key degradation processes. Direct photolysis occurs when the xenobiotic absorbs the solar light and undergoes subsequent chemical transformations. In contrast, indirect photolysis is triggered by *Photochemically Produced Reactive Intermediates* (PPRIs) that react with xenobiotics. The main PPRIs are $HO^{\bullet}$, $CO_3^{\bullet-}$, excited triplet states of Chromophoric Dissolved Organic Matter ($^3CDOM^*$) and $^1O_2$. They are formed upon absorption of solar light by photosensitizing compounds, such as CDOM, nitrate and nitrite[3]. Usually, photochemical reactions act as self-depuration processes in water bodies, but they can also induce formation of harmful photodegradation products. Luckily, the photochemical fate of xenobiotics (half-life times and photoproduction of intermediates) can be modeled, and thus foreseen, by knowing or measuring the relevant photoreactivity parameters (e.g., reactions rate constants and photoproducts formation yields) and by using suitable photochemical models[4]. Therefore, the monitoring of xenobiotics concentration in both WWTPs influents/effluents and surface waters, and the understanding of the photochemical fate of these compounds, are important tools to assess the human impact on aquatic environments. Acetaminophen (also known as paracetamol, hereafter APAP) is a widely used analgesic drug usually detected in surface waters[2] at concentrations up to 10 μg L^{-1} [5]. In this work, we have focused on the use of *Differential Pulse Voltammetry* (DPV), with a recently implemented electrochemically activated glassy carbon electrode (aGCE)[6], for the monitoring of APAP in the surface waters of the Po river basin, in the province of Turin (Piedmont, Italy). In order to confirm the reliability of the electrochemical response, we have compared DPV results with those obtained with *High Performance Liquid Chromatography* hyphenated with *High Resolution Mass Spectrometry* (HPLC-HRMS), commonly used to quantify pharmaceuticals. Furthermore, DPV with the aGCE was used to assess the photochemical degradation of APAP, and the relevant kinetic results were compared to those obtained in a previous work with a standard experimental methodology[7]. The purpose is to make it possible to monitor the APAP photodegradation, and the formation of photoproducts, in real-time by developing an adequate electrochemical set-up.

References
1. Schwarzenbach et al., Science, 2006, 313, 1072.
2. Stamatis and Konstantinou, J Environ Sci Heal B, 2013, 48, 800.
3. Vione et al., Chem. Eur. J. 2014, 20, 10590.
4. Bodrato and Vione, Environ. Sci.: Processes Impacts 2014, 16, 732.
5. Heberer et al., Toxicol. Lett. 2002, 131,5.
6. Chiavazza et al., Electrochim Acta, 2016, 192, 139.
7. De Laurentiis et al., Water Res., 2014, 53, 235.

Removal and photodegradation of glyphosate herbicide from waters using a mesoporous substrate with adsorbent properties

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Nowadays, a large amount of pesticides is used worldwide and many of these substances penetrate the soils, polluting water resources. Among these compounds, glyphosate is a non-selective herbicide recently classified as a probable carcinogen for humans (Group 2A). Conventional water treatment techniques are not effective in its removal, therefore the scientific community is exploring new approaches for the removal of glyphosate from aquatic systems.

In this work, we evaluate the adsorption and degradation properties towards glyphosate of a mesoporous silica-based support, encapsulated with iron oxides and functionalized with (3-aminopropyl)triethoxysilane (SBA-15-FexOy-NH_2). Results demonstrate the excellent adsorption performance of the SBA-15-FexOy-NH_2 towards glyphosate. Indeed, the adsorption is very fast and reaches equilibrium during the first 10 minutes of contact. Through the adsorption isotherms, the maximum monolayer coverage capacity (98 mg/g) was obtained. The adsorption properties of SBA-15-FexOy-NH_2 were also studied in the presence of high concentration of PO_4^{3-} (40 mg/L), a potential competing ion frequently present in water resources. Results indicate that the material keeps unaltered its adsorption performance, while at the same time removing PO_4^{3-} from the aqueous solution.

The presence of Fe in the substrate was intended to trigger photodegradation reactions; in particular, photo-Fenton reactions were studied at pH 3.0 and 6.5 under UVA and UVB irradiation. The most effective method was UVB irradiation at pH 6.5; these conditions allowed the successfully degradation (90%) of the previously adsorbed glyphosate. Worth noting it was observed the retention of the glyphosate by-products on the SBA-15-FexOy-NH_2 sorbent, thereby preventing the release of additional molecules into the aqueous matrix. It was shown that the photo-Fenton treatment regenerates the material and makes it possible to carry out at least three adsorption-degradation consecutive cycles, without any loss in performance.

Finally, the adsorption and photodegradation capabilities of the material have also been verified on a Po river water sample, thus showing the possible application of the sorbent even in matrices that are affected by high amounts of possible interfering species (e.g. organic matter).

The study here presented is part of a PhD research program.

Characterization of Ionic Composition in the Submicron Fraction of Urban Aerosol

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Atmospheric particles are polydisperse, varying the diameter of more than four orders of magnitude: from some nanometers (nm) to tens or hundreds of micrometers (μm)[1]. Particle size is one of the most important parameters to monitor particles' behavior in the atmosphere because it indicates the type of source and influences transport and deposition processes. Particle size distribution and concentrations of ionic species are quantified to determine their potential sources of input, chemical evolution and transport (2).

The main aim of the present work was to investigate the particle size distribution of ionic compounds (Cl^-, Br^-, I^-, NO^{3-}, MSA, SO_4^{2-}, PO_4^{3-}, C_2-oxalic acid, C_2-glycolic acid, C_2-acetic acid, C_3-malonic acid, cis-usC_4-maleic, trans-usC_4-fumaric, C_4-succinic acid, αC_7-benzoic acid, C_5-glutaric acid, hC_4-malic acid, C_6-adipic acid, C_7-pimelic acid, Na^+, NH_4^+, K^+ and Mg^+) in urban aerosol collected at Venice. We used 120 MOUDI^{TM} II sampler that permitted to separate particles in 12 dimensional fractions starting with a diameter greater or equal to 18 μm to a diameter below of 56 nm. The sampling was carried out during the 2016 spring season between March and May.

The determination of anionic compounds was performed using ion-chromatography coupled to mass spectrometry (IC-MS), while cationic species were determined through capillary ion chromatography with conductometry[2].

The concentration of ionic compounds in the aerosol samples represented the highest percentage of aerosol mass concentration. The study of the ionic composition and their particle size distribution in the analyzed samples has allowed to identify different sources, as well as marine input and anthropogenic contribution.

References

1. P. H. Mcmurry, "A review of atmospheric aerosol measurements", vol. 34, 2000;
2. E. Barbaro et al., "Particle size distribution of inorganic and organic ions in coastal and inland Antarctic aerosol," pp. 2724–2733, 2017.

Sea Salt Sodium Record from Talos Dome (East Antarctica) as a Potential Proxy of the Antarctic Past Sea Ice Extent

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Sea-ice represents a powerful phenomenon exerting a strong influence on the oceanic, biological and climatic systems and, given its importance, it is a focus in environmental research. The expansion and retreat of Antarctic sea-ice is one of the most striking seasonal changes affecting the Earth today, effectively increasing by two-fold the surface area of Antarctica. Despite an unknown exact mechanism, sea-ice plays a critical role in the polar amplification of climate change and, therefore, it is important to predict changes in sea ice under the future conditions of an ongoing climate change. A better understanding of the links between sea-ice and climate and a real improvement of the models requires a large series of long observational datasets. Antarctic sea ice has shown an increasing trend in recent decades, but with strong regional differences from one sector to another of the Southern Ocean. The Ross Sea and the Indian sectors have seen an increase in sea ice during the satellite era (1979 onwards). Here we present a record of $ssNa^+$ flux in the Talos Dome region during a 25-year period spanning from 1979 to 2003, showing that this marker could be used as a potential proxy for reconstructing the sea ice extent in the Ross Sea and Western Pacific Ocean at least for recent decades. After finding a positive relationship between the maxima in sea ice extent for a 25-year period, we used this relationship in the TALDICE record in order to reconstruct the sea ice conditions over the 20th century. Our tentative reconstruction highlighted a decline in the sea ice extent (SIE) starting in the 1950s and pointed out a higher variability of SIE starting from the 1960s and that the largest sea ice extents of the last century occurred during the 1990s. Our findings were also compared to other ice core reconstructions of Antarctic past sea-ice extent.

A Six-year Record of Size Distribution and Chemical Composition of Arctic Aerosol. Main Results and Future Bi-polar Perspetives.

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The Arctic regions are among the areas most sensitive to present climate changes; through connections involving ocean, atmosphere, biosphere, lithosphere and cryosphere, they respond to, amplify, and drive changes elsewhere in the Earth system, so that understanding their role the climate-environmental feedback processes is essential in order to set reliable predictive climate models. In particular, the atmospheric aerosol strongly interacts with the climate forcings through scattering and absorption of the solar irradiation and as sources of cloud condensation nuclei. Although these processes are well known, the quantitative and qualitative (the sign of the climate forcing) of the aerosols in the Polar Regions is affected by a large uncertainty, yet. The main uncertainties include the relative cloud/snow surface albedo and the scarce spatial coverage of size distribution and chemical composition of aerosol at high latitudes. In order to improve our knowledge on the size distribution, the atmospheric load and the chemical composition of the Arctic aerosol, continuous measurements and sampling campaigns are ongoing since 2010 in two Arctic sites: Thule (North Greenland) and Ny Alesund (Svalbard Island, Norway). At Thule, 24-h samples are all-year-round collected at daily or every other day resolution. Contemporaneously, "summer" (March to September) aerosol was annually sampled at Ny Alesund. In the latter site, aerosol was collected by several systems (PM10 samplers, multi-stage impactors (4- and 12-stage Dekati samplers) and on different substrates (Teflon filters, quartz filters, polycarbonate and Teflon membranes). Besides, shorter measurement and sampling campaigns were carried out by using a tethered balloon, up to about 1.000 m altitude, in order to study the effect of the PBL dynamics on the aerosol atmospheric load and chemical composition. Filter chemical analysis includes: ions composition (inorganic anions and cations and selected organic anions, including light carboxylic acids and MSA), elemental composition (by PIXE analysis), main and trace metals (including Rare Earth Elements - REEs, by ICP-HR-MS), Pb isotopic ratios (by ICP-QMS) and Elemental/Organic Carbon fractions (EC/OC, by Sunset thermo-optical analysis). Besides, continuous measurements of particle size-distribution (TSI-SMPS and TSI-APS; 6 nm – 20um; 10 min resolution), Black Carbon (by Particle Soot Absorption Photometry – PSAP) and natural radioactivity (Rn progeny, by FAI PBL Monitor) were carried out during the sampling periods at Ny Alesund. Here we report the most relevant results up to now obtained and the future perspective both concerning Arctic and Antarctic aerosol, in the framework of three PNRA (Progetto Nazionale di Ricerche in Antartide) projects recently approved and funded.

In particular, the use of specific chemical markers (such as nss-sulfate for anthropic Arctic Haze, REEs elements for dust, MSA for biogenic emissions, selected heavy metals for local and long-range anthropic sources) allowed studying the changes in sources intensity and atmospheric transport efficiency for aerosol reaching the Arctic regions. Sulfate source apportionment was performed in order to evaluate the contribution of sea spray, continental dust, biogenic emissions and anthropic activities to the sulfate global budget. MSA was used in order to understand the complex interactions among sea ice dynamics, chlorophyll blooms and marine primary productivity. Lead isotopic composition and REEs composition were used in identifying the continental source of dust and anthropic pollutants. Finally, a relationship between marine biogenic emissions and nucleation events was found by particle size distribution in the nanometric mode.

Effects of Biomass, Temperature and Thermochemical Process on PAH Concentration in Biochar

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Biochar is the solid carbonaceous material produced by the pyrolysis of biomass for a variety of applications in the agro/environmental field[1]. The thermochemical processes of biomass also produce a variety of organic compounds including PAHs, highly harmful compounds to man and to the environment.

The effects of biomass, temperature and type of process (pyrolysis and gasification) on 16 US EPA PAH concentration in biochar were investigated. To this end, 47 biochars were analyzed for their PAH content. 38 of them were produced in laboratory furnace, in highly controlled pyrolysis conditions, from 11 biomasses of which 7 were of wood (beech, chestnut, pine, poplar, spruce pine, commercial conifer, and pruning from fruit tree and grape vine) and 4 of grass (thistle, giant cane, rice straw and miscanthus leaves). The temperatures of pyrolysis were 350, 550, 750 and 1000 °C. In addition, 6 biochars were produced in industrial plants of pyro-gasification or pyrolysis. These plants were fueled with six of the biomasses used in the laboratory pyrolysis (spruce pine, conifer, pruning, thistle, giant cane and rice straw). Finally, 2 biochars (named STG and SPG), produced in a small experimental plant of gasification, and a biochar commercially available were considered. For the latter the production conditions were not known.

Examining the sum of the concentrations of 16 PAHs (Σ_{16}PAH) of each laboratory biochar, it can state that the type of biomass (wood or grass) does not affect the Σ_{16}PAH, but this Σ_{16}PAH depends on single biomass. Although the highest Σ_{16}PAH values related to the type of biomass were found at 350 °C for wood biochars and 550 °C for grass biochars. The Σ_{16}PAH at the highest temperatures studied (750 and 1000 °C) were always lower than values of the other temperatures. Other interesting considerations that can be made concern single PAHs trapped on biochar at 350, 550 and 750 °C. For instance, all 16 PAHs were present at 550 °C except acenaphthene, and naphthalene and phenanthrene were found to be the most common and abundant PAHs. The process (pyrolysis or gasification) influences on the concentration of PAHs in biochar, however, the design of the reactor used and the working temperature are also important. The fact that the produced gas passes through or not the char bed to exit from reactor is an important factor. The lab. pyrolysis, in which the produced gas is continuously brought away by inert gas, gave biochar with Σ_{16}PAH lower than pyro-gasification, in which the syngas passes through the char bed. For example, Σ_{16}PAH were 455 and 3989 µg/kg for lab. pyrolysis and ind. pyro-gasification biochars, respectively. In this study the ind. pyro-gasification biochars were generally characterized by PAHs that did not include those with MW > 228 uma, unlike the biochar from ind. pyrolysis that contained 15 of the 16 US EPA PAHs. Considering the TEC (toxic equivalent concentration) values, the ind. pyro-gasification biochars investigated are suitable for their potential use as soil amendments.

In conclusion, it can be said that to produce biochar with lower PAH content is necessary choose the suitable parameters concerning the feedstock, temperature, process and design of the reactor.

Reference

1. M. Ghidotti, D. Fabbri, A. Hornung, Profiles of Volatile Organic Compounds in Biochar: Insights into Process Conditions and Quality Assessment, ACS Sustain. Chem. Eng. 5 (2017) 510–517. doi:10.1021/acssuschemeng.6b01869.

Particulate and gaseous indoor contamination at the Museum of "Last Supper" of Leonardo Da Vinci: results from one year of monitoring activity

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Atmospheric particles and gaseous pollutants can affect cultural heritage, especially the most fragile, such as The Last Supper of Leonardo da Vinci. During the centuries, The Last Supper became a case in establishing the extent of the issue of environmental conditions for the preservation of the Leonardo's masterpiece. The Leonardo's painting is protected by a filtering system[1]. Previous indoor studies in the Last Supper museum were aimed to the indoor/outdoor penetration of particulate matter[2]. Uncertainties concerning the particles dynamics and the gaseous contamination still persist. At this purpose, a specific experimental setting was developed allowing to perform continuous, high-time resolution, monitoring activity: a novelty in the field of conservation of cultural heritage.

Measurements (March 2016-April 2017; 1 min time res) were conducted using a combination of: 1) Aethalometer (AE-33, Magee Scientific, 7-λ), 2) condensation particle counters (TSI 3787), 3) an optical particle counters (Grimm 1.107), 4) a low volume sampler (Mega system) 5) a custom developed rotating impactor, 6) a real-time NH_3-NO_x-O_3 detector (Environment spa) and 7) passive and active CO_2, samplers were used in order to determine the isotopic ratio $^{13}C/^{12}C$ ($\delta^{13}C$) using a newly developed method[3]. A Ca-based sorbent, $CaO/Ca_{12}Al_{14}O_{33}$, 75:25 w/w, was used for passively collecting atmospheric CO_2, and an Ascarite®-based sorbent for the active sampling; the collected CO_2 was desorbed from the substrate with acid treatment and directly analysed by non dispersive infrared spectroscopy (NDIRS).

Whereas particles concentrations reached the low level reported in previous studies[1], the high time resolution showed their diurnal cycle: the total number concentration reached a value of 20.7 ± 0.1 cm^{-3} (BC was 8 ± 1 ng m^{-3}) during night and then increased with visitors up to 167.8 ± 3.3 cm^{-3} (BC was 37 ± 4 ng m^{-3}) during daytime. These values remained however far from outdoor pollution levels (~$1\text{-}2*10^4$ cm^{-3} and ~1000-2000 ng m^{-3}) highlighting the efficiency of the filtering system. The impact of visitors was also confirmed by CO_2 data that revealed a decreasing $\delta^{13}C$ values with increasing the number of visitors. The results on the isotopic composition of CO_2, correlated to the variation of atmospheric CO_2 concentration, permitted to follow the anthropogenic impact in the different areas of museum and were used such as a non-invasive marker to detect the air circulation and to improve the filtering system operations.

The diurnal cycle of primary and secondary particles was also investigated obtained using the apportionment of particle concentration based on N/BC ratio[4]. A secondary particles peak in the afternoon (up to 300 m^{-3}) was observed. Also the NH_3 concentration peaked in the afternoon reaching a double concentration than that observed during night-time.

Moreover, the chemical composition of collected PM samples showed a mass fraction of NH_4NO_3 of 7% inside the museum that, compared with the external value of 30% highlighted the volatilization and decomposition of NH_4NO_3. The presence of ammonia became a driver of new particle formation.

References
1. Gasparini F., Stolfi G., Il Cenacolo Vinciano: impiantistica e microclima all'interno del Refettorio., 2014;
2. Daher et al., Environ. Sci. Technol., 2011, 45 (24), pp 10344–10353;
3. R. Cucciniello et al;. Atmospheric Environment 60 (2012) 82-87;
4. Reche at al., Atmos. Chem. Phys., 11, 6207–6227, 2011.

Comunicazioni Poster

Analytical Investigation on Archaeological Patina: A Tool to Shed Light on the Provenance of Ancient Bronze Coins

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The elemental composition of archaeological patina of ancient bronze coins is very complex and it results from the deterioration processes, generically named "corrosion", that occur during the centuries. The corrosion products covering the coins are strictly correlated to the environmental characteristics of the burial site. So the analysis of coins surfaces can be a useful tool for numismatists to verify the provenance of coins: a different surface composition of similar bulk materials could be probably due to different micro-environmental conditions[1,2,3]. The aim of this study was to verify whether a set of 117 ancient bronze coins of the Roman Empire period that was declared to be found during surveys on Cesén mountain (North-eastern Italian Alps) could be compatible with another set of 103 coins coming from the archaeological excavation carried out thereafter in the same area. To avoid the damage, non-destructive analytical techniques were used to characterize the surface of six coins taken blindly from the two sets in order to highlight similarities and differences between the samples. On the other hand, some soil samples collected in the archaeological site were analysed to verify whether the patina layer of all coins could contain chemical components compatible with the elemental composition of soil. The elemental analysis of the patinas was carried out by micro-X-ray fluorescence spectroscopy (µ-XRF). To better observe the morphology of corroded surface, scanning electron microscopy coupled to energy dispersive spectroscopy (SEM-EDS) was used. Then corrosion compounds covering the coins were identified recording ATR-FTIR (attenuated total reflectance-Fourier transform infrared spectroscopy) spectra. Soil samples were analysed without pre-treatment by means of XRF and, after acid digestion, by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES). The bulk composition of coins was specific of different coinage periods, whereas some elements unexpected in the metal alloy were found only on the surface of two coins, in particular Ti and Mn that were also found in soil samples. This result, together with the morpho-chemical investigation, lead us to subdivide the six coins into two groups, each containing two and four coins: this grouping corresponded respectively to the set of coins coming from the archaeological site and the set of survey. The group of four coins seems not to show the characteristics of coins exposed to soil for long periods of time: patina and corrosion products could suggest a different provenance (restored finds or even a hoard). Analytical results of this study support numismatists who were not convinced of considering all coins coming from the same site on the basis of archaeological documentations. For this reason, they will not take into account all the coins to develop interpretive hypotheses but only those coming from archaeological excavations.

References
1. L. Robbiola, J.M. Blengino and C. Fiaud; *Corrosion Science*, 1998, *40* (12), 2083-2111.
2. L. Pronti, A. C. Felici et *al*.; *Appl. Phys. A*, 2015, 121, 59–68.
3. R. Reale, S.H. Plattner et *al*.; *Chem. Cent. J.*, 2012, 6(Suppl 2): S9.

Characterization of Brass Alloys After Different Cleaning Methods by XPS and XAES.

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In the frame of the projects on the sustainability in cultural heritage[1,2], an interdisciplinary methodology has been developed for the evaluation and monitoring of the corrosion state of the inside of historical brass instruments before and after being played. There is the need to establish a protocol for preventing the damage of the instruments.

During their usage, the inner walls of the instruments get in contact with humid air, sweat and saliva. A contamination layer and a thin oxide film or a layer of corrosion product, called patina, is formed. As the acoustic properties of the instruments depend on the material composition the patina and corrosion products may compromise the quality of the sound. Thus, the brass surface has to be cleaned without changing the performance of the instruments. The aim of this work is to compare different ways to remove the patina of ancient brass musical instruments. A series of brass model alloys with a zinc content ranging between 18 and 37 wt% and some pieces obtained from old destroyed instruments, supplied by the Bern museum, have been characterized by X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES) before and following the surface cleaning i.e. after mechanical polishing, cleaning with Metarex®, ultrasonic cleaning in distilled water and cleaning with organic solvents (butan-2-one, propan-2-one and ethanol). The chemical state identification and the quantification of copper and zinc have been obtained on the basis of the binding and the kinetic values of the Cu2p, $CuL_3M_{45}M_{45}$, Zn2p and $ZnL_3M_{45}M_{45}$ peaks. The results showed that on the surface of as received samples as well as after washing with distilled water, no signals from metallic Cu and Zn were observed, thus indicating that the oxide and the organic layer were thicker than the XPS sampling depth[3]. Based on the assignment of the Wagner chemical state plot[4] $Cu(OH)_2$, Cu_2O and $Zn(OH)_2$, probably in the form of hydrozincite, were identified. After cleaning with organic solvents, the intensity of the C1s peak decreased and the metallic components of Cu and Zn signals were revealed. The line shapes of Cu2p and Zn2p signals were similar to those found on mechanically polished brasses. Cleaning with organic solvents did not affect the oxide composition. Cu_2O and ZnO are found to be the main compounds of the outermost layer of the mechanically polished brasses. After cleaning with Metarex® only a very thin zinc oxide layer together with an organic hydrophobic layer of about 3 nm thickness was detected. The analytical approach used during this work allowed the identification and the quantification of the species present at the surface of the brass alloys after different surface treatments and all the results will be presented and discussed.

References
1. "Brass instruments of the 19th and early 20th centuries between long-term conservation and use in historically informed performance practice"; Swiss National Science Foundation (SNF) CR12I1_146330/1.
2. Sustainability in cultural heritage PRIN MIUR 2010-2011.
3. F. Cocco, B. Elsener, M. Fantauzzi, D. Atzei, A. Rossi; *RSC Advances*, 2016, *6*, 31277–31289.
4. C.D. Wagner; *J. Vac. Sci. Technol*., 1978, *15*, 518.

Elucidation of Rituals and Food in the 'Cult Area' of Roca Through Chemical Analyses

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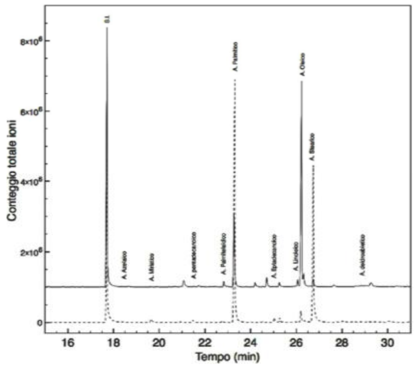
The application of analytical chemistry to archaeological research has increased substantially over the last half-century and today represents a major methodological subfield within archaeological science[1,2]. The paper reports the results obtained onto a selection of Final Bronze Age ceramic materials from Bronze Age site of Roca.

Two *pithoi* in fine fabric -*figulina*- and five vessels in coarse fabric -*impasto*- (one *olla*, one dipper, three small cups) have been selected and analyzed. Regarding the archaeological contexts of provenience, one *pithos* comes from the so called *Capanna-Magazzino* located in SAS VI and all the other materials come from the South-East sector of the so called *Capanna-Tempio* located in SAS IX.

Using high temperature gas chromatography and compound specific isotopic ratio, it has been possible to identify different types of lipids absorbed by the ceramic core[3]. The *pithos* from the *Capanna-Tempio* shows residues of lipids clearly identified as olive oil. The *olla* and the dipper show residues of lipids referable to non-ruminant animals. One of the three small cups does not contain any traces of lipids but quantities of beeswax and some evidence of conifer's resins. Two cups contain residues of animal lipids that can be attributed to ruminant animals, particularly to sheep.

The *pithos* from the *Capanna-Tempio* demonstrates processes of accumulation of huge quantities of olive oil in a ritual context characterized by precise comparisons with the Bronze Age Aegean. The traces of resin in the *pithos* from the *Capanna-Magazzino* could be interpreted both as results of surface treatment or as residues of various contents different from olive oil, such as flavored wine. The animal lipids found in the *olla* seem to confirm the use of this shape in food-preparing activities.



References
1. Colombini M.P., Modugno F. 2009, Organic mass spectrometry in art and archaeology, John Wiley & Sons, Ltd.
2. Evershed R.P., Dudd S.N., Copely M., Berstan R., Scott A., Mottran H., Bulley S., Crossman Z. 2002, Chemistry of Archaeological Animal Fats, Accounts of Chemical Research 35, 8, pp. 660-668.
3. Guglielmino R., Maggiulli G., Pagliara C., Rugge M.; "Indizi di comunanza di culti e di riti tra genti indigene ed egee"; in Radina F., Recchia G., a cura di 'Ambra per Agamennone', Bari, 2010, pp. 129-132.

Development of Chromatography–Atmospheric Pressure Ionization–Mass Spectrometry Methods for the Simultaneous Analysis of Different Lipid Classes Within Archaeological Finds

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The ability of our ancestors to fulfil their basic nutritional needs was a factor that shaped the evolution of modern man and the societies that followed. There is an increasing amount of evidence showing that organic residue analysis (ORA) is able to address many archaeological questions about past diets, ancient practices, early use of natural substances, but also vessel production and related use[1]. Most of the organic residue analysis have been performed on absorbed material recovered from archaeological finds, like pots and vessels[2]. Ceramic materials represent an ideal environment for the survival of residual organic matter, because its absorption into the microporous structure prevents from long-term degradation. In fact, some investigations have shown that possible contamination arising from migration of soil components, or compositional alterations through microbial activity, are minimal for compounds absorbed in potsherds[3]. Hence, these residues are a direct reflection of the original contents and usage of ceramic vessels. On these basis, this project aim is to develop chromatographic/mass spectrometry based analytical methodologies to identify the organic pyrolysis products that reside within pots used for food storage, or within hearths following the cooking of different foodstuffs. Different instrumental approaches and protocols have been developed to determine the optimal chromatograhic and/or mass spectrometric approaches to study a range of expected lipid families. These include fatty acids (FAs), fatty acid methyl esters (FAMEs), triacylglycerides (TAGs), sterols and stanols. The selective ionisation processes offered by different atmospheric pressure ionisation techniques have been utilised and shotgun analysis using ultrahigh resolution mass spectrometry methods have been compared with modern LC-MS approaches (UHPLC-MS and UHPSFC-MS). Initially, standard compounds and compound mixtures have been used, including addition of surrogate matrices representing the composition of the actual samples. The developed methods proved to be accurate (bias%<15%), precise (CV%<10%) and with high detectability (down to 1 ng/ml), thus suitable for the analysis of trace level compounds in archeological matrices. The combined use of the SIR detection mode and the high resolution ensured high selectivity and the possibility to discriminate isobaric compounds, species having the same retention time but different m/z ratio and identify molecules whose the corresponding analytical standard is not available. These protocols have been tested successively for the analysis of residual organic materials produced from a cooking hearth, with different animal/vegetable products, or present within pots. The final aim was to identify food/diet related chemicals whose qualitative and quantitative composition might represent a biomarker able to provide information related to past human activity.

References
1. Shillito L. M., Almond M. J., Wicks K., Marshall L. J. R., & Matthews W.; "The use of FT-IR as a screening technique for organic residue analysis of archaeological samples"; *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2009, *72*(1), 120-125.
2. Copley M. S., Bland H. A., Rose P., Horton M., & Evershed R. P.; "Gas chromatographic, mass spectrometric and stable carbon isotopic investigations of organic residues of plant oils and animal fats employed as illuminants in archaeological lamps from Egypt"; *Analyst*, 2005, *130*(6), 860-871.
3. Evershed R. P., Heron C., & Goad L. J.; "Analysis of organic residues of archaeological origin by high-temperature gas chromatography and gas chromatography-mass spectrometry"; *Analyst*, 1990, *115*(10), 1339-1342.

SWIR Imaging for Cultural Heritage: An Innovative Spectroscopic Method for the Study of Bronze Artworks

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In the past decades, infrared reflectance spectroscopy has been largely applied in analytical investigations of heritage materials. In particular, the production of compact systems allowed the establishment of the technique as one of the most suitable approaches for non-invasive studies on artworks by using both the mid-infrared (MIR, 4000-400 cm^{-1}) and the near-infrared (NIR, 10,000-4000 cm^{-1}) ranges. However, drawbacks related to the distortion of bands in the MIR range – mainly induced by specular reflection – have been widely reported in several research works. On the other hand, spectroscopic investigations in NIR range, characterised by the presence of overtone and combination bands, offer the possibility to obtain weaker but not distorted IR signals, providing important information for the identification of artistic materials.

To deeply evaluate the applicability of advanced methods in infrared spectroscopy, based on the use of the NIR range, a new short-wave infrared (SWIR) hyperspectral imaging (HSI) system was proposed for the study of outdoor and archaeological bronzes, whose thorough characterization still represents a crucial issue in heritage science. The sensor works in the 1000-2500 nm spectral range, with line-scan mode, and a spatial resolution < 1 mm. Indeed, bronze surfaces are highly complex and instable systems. In particular, the surface of bronze artworks usually interacts with the surrounding environment and gradually develops brown and green patinas due to the formation of corrosion products. To protect the degraded external surface of bronzes, several organic materials (natural or synthetic) are often applied. As a result, the composition of the external surface of either outdoor or archaeological bronzes results highly heterogeneous. The correct identification of all the components are fundamental to define the state of conservation of metal artworks, addressing proper restoration actions.

These advanced methods were tested on outdoor bronze specimens, as well as on archaeological Chinese coins from the Northern Song Dynasty (960-1127 A.D.). Suitable chemometric methods were deployed to correctly process hyperspectral data.

The results showed as the SWIR HSI system, coupled with chemometric data processing, was able to efficiently identify degradation products (such as brochantite, malachite, silicates and azurite), as well as organic coating products, such as waxes and Incralac™. The possibility of spatially localising such compounds across sample surfaces, provided by the potential of the imaging system, resulted a feature of definite interest for both conservation and restoration purposes.

Investigation of Modern Inks in Felt-tip Pens

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Inks of felt-tip pens are used by modern artists for the realization of sketches, drawings, copies, architectural drawings and other technical designs. However, these inks are usually very sensitive to light and chemical agents and the exact knowledge of their composition may be important to define the optimal conservation treatment and/or storage conditions. So far, few studies have been addressed to the chemical characterisation of these materials[1] and often information on binders, fillers, dyes and pigments is lacking.

In this study felt tip pens (Faber-Castell) used by the French modern artist Anne Flore Cabanis and other artist pens (Stabilo) were investigated by using an integrated analytical approach. The inks have been analysed with Fourier transform infrared (FT-IR), μ-Raman and visible reflectance spectroscopy, and pyrolysis - gas chromatography - mass spectrometry (Py-GC-MS). The Raman spectra of the Faber-Castell inks clearly show the presence of phthalocyanine, dioxazine and azo pigments. The Stabilo inks, instead, contain mixtures of dyes as evidenced by thin layer chromatography (TLC). Surface-enhanced Raman spectroscopy on the TLC spots allowed to identify triarylmethane dyes[2], rhodamine B and tartrazine. (Py-) GC-MS and FTIR spectroscopy provided data on binders, solvents and additives and confirmed the identifications of the pigments and dyes.

Since the photosensitivity of this type of inks is usually very high, a preliminary investigation on accelerated ageing on some ink samples was carried out. Spectroscopic techniques were used for the monitoring of photo-degradation.

References
1. F. C. Izzo, V. Vitale, C. Fabbro, H. Van Keulen; *Microchemical Journal*, 2016, *124*, 919.
2. Y. Cheng Ho, W. W. Y. Lee, S. E. J. Bell; *Analyst*, 2016, *141*, 5152.

An XPS Study of Stones Degradation Using a Reference Gravina Tuff Placed Outdoor Under Specified, Environmental Conditions

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Within a current National Smart Cities (SCN_00520) project, entitled '*Product and process innovation for maintenance, preservation and sustainable programmed restoration of Cultural Heritage'*[1], the use of XPS (X-ray Photoelectron Spectroscopy) as a surface-specific technique, in combination with complementary surface and analytical techniques, is aimed at contributing to the diagnostic phase of the project whose procedural accuracy is essential to set intervention priorities. Since deterioration of any kind, due to ageing, natural or anthropogenic factors, begins from surface reactions, XPS can be suitably employed for the ex-situ compositional characterization of degraded compounds properly scraped from surfaces. The present contribution is focussed on the study of the main degradation products forming on stones constituting artifacts/monumental buildings in the areas of cultural heritage belonging to the municipalities of the Basilicata region. In particular, it was intended to complete the surface characterization provided by combined surface techniques[2] of a reference sample, properly sized (about 1m[3]), using Gravina calcarenite stones, and placed in a site with reported coordinates in the industrial area of S. Nicola di Melfi. In the previous work, the effect of local environments on its North, South, East and West surfaces was evaluated after three and six months of exposition, revealing already incipient degradation also influenced by the exposition side[2]. Here, we show the elaboration of additional XPS data acquired over an extended period, using the same curve-fitting procedure[3], as before. The whole data set will then be statistically interpreted for attempting a better rationalization of the alteration phenomena due to concomitant ageing, natural or anthropogenic factors occurring in real situations.

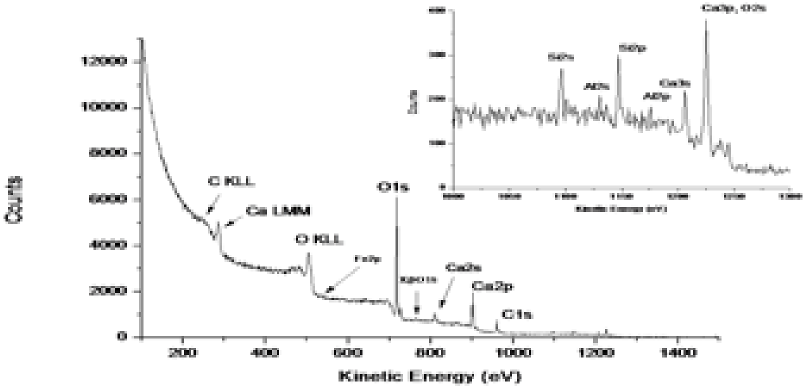

Figure 1. A wide XPS spectrum of the 'as prepared' reference sample, taken from reference 2

References
1. International IUPAC Conference on Green Chemistry, 4-8 September 2016, Venice (Italy).
2. Scrano L., Fraddosio-Boccone L., Langerame F., Laviano R., Adamski Z., Bufo S.A.; *Karaelmas Science and Engineering Journal 1*, 2011, *2*, 1-14.
3. J. E. Castle, A.M. Salvi; *Journal Electron Spectroscopy and Related Phenomena*, 2011, 114-116.

Mobility of Trace Elements at the Sediment-Water Interface in Two Tourist Port Areas of the Gulf of Trieste (Northern Adriatic Sea)

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One of the main environmental issues affecting the coastal marine environments is the accumulation of contaminants in sediments and their potential mobility. The sediment acts as a sink for many chemical species (metal(oid)s, PAHs, PCBs etc.). However, this situation can be only temporary since early diagenesis biogeochemical processes can recycle these contaminants which may subsequently accumulate along the aquatic trophic chain. In this work, *in situ* experiments were conducted at two tourist ports (marinas) located in the Gulf of Trieste (northern Adriatic Sea), one in Slovenia and one in Italy. The latter is well known to be a site contaminated by long-term shipbuilding activities. The main aim was to understand if and where recycling at the sediment-water interface (SWI) may affect trace metal(oid)s. A benthic chamber, successfully used in other works in the same Gulf [1,2], was employed. Water sampling was performed during a 8-hour period to measure trace metal(oid) concentrations with time. Short sediment cores were collected near the chamber to investigate the solid (sediments) and dissolved phases (porewaters). Both diffusive and benthic fluxes were estimated to elucidate the release of trace metal(oid)s at the SWI. Total trace element concentrations were determined following a complete mineralization of the sediment (*aqua regia* + HF), whereas a weak extraction with diluted HCl (0.5 M) was carried out to quantify their potential "bioavailable fraction". Quantitative analyses were performed by ICP–OES on sediment mineralized solutions and by ICP–MS on porewater and benthic water samples. Total element contents in sediments, resulted up to two orders of magnitude higher in the Italian marina (0.4 %Pb, 0.15% As and Cu, 0.25% Zn) than in the Slovenian one, confirming the high contamination level of this site. Despite this heavy contamination, the "bioavailable fraction" of metal(oid)s extracted was scarce or null. Conversely, sediments from the Slovenian site showed high percentages of the extractable fraction from 4% (Cr) to 82% (Cu) of the total content. Trace metal vertical profiles in porewaters showed a clear diagenetic sequence. The suboxic/anoxic conditions of sediments allowed the dissolution of Fe and Mn oxy-hydroxides, thus enhancing the concentrations in porewaters of Fe, Mn and other associated trace metal(oid)s. However, the diagenetic sequence and the suboxic/anoxic transition were highly dependent on the characteristics of each site. Maximum concentrations of dissolved Fe, Mn, Pb and Zn were found in the first centimeters of one site of the Italian marina where sediments became quickly anoxic with depth. Conversely, in the Slovenian marina and in the second Italian site, the highest concentrations were recovered from the deepest porewater layers, especially for Fe (up to 2.5 and 7.7 mg L^{-1}, respectively). Positive effluxes were observed for Mn, Pb, Zn and V in the Italian marina whereas for Cu and Ni were most notably in the Slovenian marina and for as at both sites. Hg fluxes were low in spite of its high concentrations (up to 1000 mg kg^{-1}) in sediments of the Italian site. In general, benthic fluxes of metal(oid)s at the SWI can be partially explained by considering the dissolution of Fe/Mn oxy-hydroxides and metal speciation in bottom sediments. The results suggest that although the bottom sediments of the Italian marina exhibit the highest trace metal(oid) concentrations, they are scarcely remobilizable. On the contrary, in the Slovenian marina, sediments seem to be comparatively a significant source of trace elements (except for Fe, Pb and V) in the water column as consequence of diagenetic processes at the related interface.

References

1. Bertuzzi et *al.*; 1997; doi:10.1023/A:1018398231038.
2. Covelli et *al.*; 1999; doi:10.1006/ecss.1999.0466.

Iron Speciation in Antarctic Sea-Water and Sea-Ice: Significance and Analysis

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Iron is considered the most important trace element in the ocean for the growth of marine organisms and a key factor in regulating primary productivity in many areas of the world's oceans. In fact, it is involved in several metabolic pathways including biosynthesis of chlorophyll, transport of electrons through the photosynthetic and respiratory transport chains and nitrate assimilation by phytoplankton. Since marine phytoplankton can convert dissolved carbon dioxide into organic matter through photosynthesis, the iron limitation may have important implications for air-sea exchange of carbon dioxide and consequentially on global carbon and Earth's climate. This is particularly clear in remote regions like the Southern Ocean, since sea-ice contains high concentrations of iron and represents one of the most important sources of this nutrient in polar waters through melting during spring. Over 99% of the dissolved iron in the ocean is bound to organic ligands, making algal growth limited not only by a general lack of this element, but also by the bioavailability of organically bound iron.

In order to improve the understanding of iron biogeochemistry and to predict how marine productivity in polar waters can be affected by future changes, it is crucial to provide analytical methods which can detect low levels of iron in sea-water and sea-ice with high precision and accuracy, as well as to determine the amount and strength of iron-binding organic species.

In this work, we present the procedures used by our group for iron speciation in Antarctic sea-water and sea-ice. For the determination of total dissolved iron in sea-water, a low-blank pre-concentration procedure based on magnesium hydroxide co-precipitation followed by inductively coupled plasma mass spectrometry (ICP-MS) was developed. Iron speciation was determined by adsorptive cathodic stripping voltammetry (AdCSV) using a competitive ligand. This is the only technique to obtain the concentration of iron-binding ligands and their stability constant.

The described procedures were applied to samples collected during international surveys carried out in the Southern Ocean. The data collected provide paramount information on the iron sources and on the mechanisms controlling the bioavailable iron species in Antarctica.

Identification of Photodegradation Products of Alpha-Cypermetrin in Paddy Water by UHPLC-QTOF MS/MS

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Nowadays an extensive use of pesticides has been registered in order to limit specific class of pest proliferation in rice crops. This study regards αlpha-cypermethrin (α-CY), a synthetic pyrethroid insecticide, and its commercial formulation, CONTEST®, containing 14.5-15% of α-CY (w/w, water dispersible granule). Although the World Health Organization considered α-CY as moderately hazardous, other recent studies reported that neurotoxic effects could take place in humans[1]. Often degradation processes due to sunlight irradiation, hydrolysis or interactions with other compounds naturally present in paddy water, can give rise to new species that could be even more toxic than their precursors[2]. This study is focused on the natural photodegradation of α-CY and CONTEST® dissolved in paddy water, in order to better simulate their behavior in the real situations in paddy fields. Both solutions were subjected to solar box irradiation, setting temperature and intensity values to simulate sunlight conditions typical of the period in which paddy fields are submerged by water. The identification of the degradation products was achieved by a non-target approach (in Data Dependent Acquisition mode). To this purpose a new and sensitive ultra-high-performance liquid chromatography (UHPLC) coupled with a quadrupole-time of flight (QTOF) high-resolution mass spectrometry method was developed and validated. The elucidation of the unknown chemical structures of photodegradation products was carried out by using the elemental composition (tolerance <5 ppm), the relative abundance of the isotopic cluster (tolerance of 10%), the number of rings and double bonds (RDBs), the high-accurate and high-resolution MS/MS acquired spectra, from which it was possible to obtain the elemental composition for each product ion (within an average mass tolerance of 6.4 ppm). α-CY photoproducts are mainly due to the ester bond cleavage: a group of photodegradation products maintains the phenoxybenzene core, whereas another group conserves the remaining moiety of the molecule characterized by the cyclopropane core. The irradiation of α-CY in paddy water gave rise to eight degradation products, three of them have been identified for the first time, while CONTEST® solution led to nine degradation products, six of them common to those identified for the α-CY solution and two never identified before. Hydrolysis studies of α-CY in paddy water solutions, demonstrated that α-CY concentration decreases of about 63% in a month, giving rise to 3-phenoxybenzoic acid. On the contrary, CONTEST® solution showed a lower hydrolysis rate than standard α-CY, probably because of the stabilizing effect of the co-formulants present in the commercial product. Ecotoxicological tests were performed on α-CY and CONTEST® solutions, both before and after irradiation; they showed a similar toxicity of all the tested solutions. Mutagenicity of the photoproducts was evaluated through an EPA QSAR approach, by the simulation of a virtual Ames test[3]. The results were positive for three out of eleven degradation products, indicating that those degradation products are more hazardous than α-CY, hence particular attention must be paid on the use of this insecticide.

References
1. D. E. Ray, J. R. Fry; *Pharmacol. Ther.*, 2006, 111, 174.
2. F. Gosetti, U. Chiuminatto, E. Mazzucco, R. Mastroianni, B. Bolfi, E. Marengo; *Environ. Sci. Pollut. Res.*, 2015, *22*, 8288.
3. https://www.epa.gov/sites/production/files/2016-05/documents/600r16058.pdf

Detection of Herbicides by Calix[6]arene-Based Fluorescent Sensors

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Diquat (DQ) and Paraquat (PQ) are non-selective contact herbicides widely used in agriculture. Numerous methods have been developed to monitor and control DQ and PQ in the environment, food, and clinical samples, including chromatography and hyphenated techniques, voltammetry and immunoassay[1]. In the last decades, many efforts have been focused on the design of supramolecular fluorescent sensors[2], which provide selectivity, sensitivity and ease of use in the detection of analytes. In the present study, we have designed calix[6]arene derivatives[3] bearing a fluorescent probe (naphtalenyl **1** or anthracenyl **2**) at the *endo* rim (Fig. 1)[4].

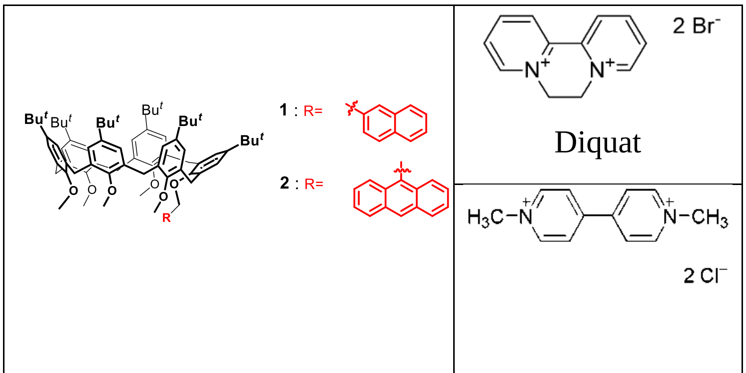

Fig. 1. Fluorescent calixarene hosts **1** and **2**.

The recognition abilities of **1** and **2** toward PQ and DQ was first investigated by fluorescence emission spectroscopy in a solution of chloroform-methanol 1:1 in order to determine the binding constants (5). Addition of PQ to a $CHCl_3$/MeOH solution of calixarene (**1** or **2)** resulted in a drastic decrease of the emission intensity of the host (Fig. 2). The resulting emission spectra of **1** in the presence of PQ exhibited a quenching of the fluorescence of **1** at micromolar concentrations of PQ guest (inset in Fig. 2). The fluorescence quenching value showed a good linear relationship with PQ concentration from 4 to 120 μM (1.0 - 30.8 mg/L) with a detection lim
μg/L, 45.5 μg/L and 25.□□μg/L for the PQ-**2**, DQ-**1** and DQ-**2** syst
potential method for detection of PQ and DQ by calixarene-based fluor

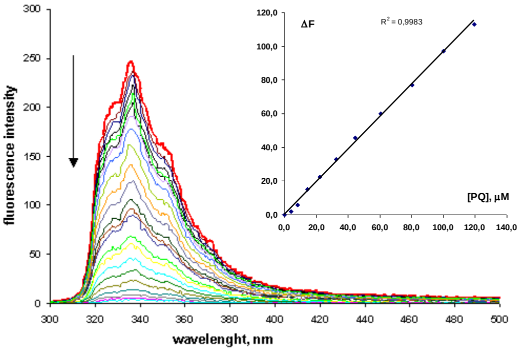

Fig. 2. Fluorescence quenching of **1** by increasing [PQ] in chloroform-methanol 1:1 solution at 298 K. Inset: Fluorescence change of **1** vs [PQ]

References
1. O. Nunez et al, J. Chromatogr. A 946 (2002) 275–282; J-M. Zen et al. Anal. Chem. 1996, 68, 498-502; C. Mastichiadis et al., Anal. Chem. 74 (2002) 6064–6072; Bacigalupo, M.A. et al.. J. Agric. Food Chem. 2005, 53, 216.
2. Lavigne, J. J., Anslyn, E. V. ; *Angew. Chem., Int. Ed.*, 2001, *40*, 3118–3130. Lehn, J.-M. Supramolecular Chemistry: Concepts and Perspectives, VCH, New York, 1995. Steed, J. W.; Atwood, J. L. in Supramolecular Chemistry, Wiley, 2009.
3. Calixarenes and Beyond; Neri, P., Sessler, J. L., Wang, M.−X., Eds.; Elsevier: Oxford, 2016. Gutsche, C. D. Calixarenes, An Introduction; Royal Society of Chemistry: Cambridge, UK, 2008.
4. Manuscript in preparation.
5. Connors KA. Binding Constants: The Measurement of Molecular Complex Stability. Wiley; New York: 1987.
6. G. L. Long, J.D. Winefordner, Anal. Chem. 55, 7, 1983, 712A.

The Use of Scallop Shell Powder as Biosorbent for the Removal of Cd^{2+} and Ni^{2+} from Natural Waters

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Intensive shellfish production generates a large volume of preconsumer and postconsumer residue, the largest proportion of which consists of shells. This material is commonly regarded as waste and its improper disposal not only results in a waste of natural resources but also can pose environmental problems. Bivalve shell is formed by biomineralization and consists mainly of $CaCO_3$ with a small amount of organic matrix, giving it a potential for use as raw material. Recycling shell waste could potentially eliminate the disposal problem, and transform a waste into high value-added products. The present study describes the use of bivalve shell, as adsorbent material for the removal of heavy metal cations from water. Heavy metals are indeed common pollutants of natural waters, especially in the proximity of mining sites and metalworking industries. In particular the adsorption behavior of two different metals is investigated: cadmium and nickel. Cadmium is toxic for humans and biota even at low concentrations, due to the fact that being a divalent cation it can substitute calcium and zinc in biological processes resulting in the alteration of cellular metabolism[1]. Because of its toxicity the limit for potable water is established at 0.003 mg/l [2]. Nickel is widely used by industries for the production of stainless steel, Ni-based alloys and Ni-based rechargeable batteries. The extensive use of nickel compounds can cause severe environmental pollution and health problems in case of exposure to high concentrations of Ni [3]. The first part of this research project was focused on the characterization of the adsorbent material, in order to determine its chemical composition and its structure and dimension using different techniques such as inductively coupled plasma, X-ray powder diffraction, scanning electron microscopy and dynamic light scattering. Batch experiments were carried out by placing in contact a given amount of shell powder with a solution containing a known concentration of metal cations. After equilibrium was reached the solution was filtered and analyzed with inductively coupled plasma atomic emission spectroscopy to quantify the amount of not adsorbed cation. Kinetic and thermodynamic properties of the biosorbent, regarding cadmium and nickel adsorption, were investigated and the kinetic equation and adsorption isotherms describing the process were obtained. The effects of some parameters as pH, temperature and salinity were also investigated to better understand the adsorption mechanism. Finally, the competition of nickel and cadmium in the adsorption onto bivalve shell powder has been evaluated.

References
1. M. Remelli, V. M. Nurchi, J. I. Lachowicz, S. Medici, M. A. Zoroddu, M. Peana; *Coordination Chemistry Reviews*, 2016, 327-328, 55-69.
2. “Cadmium in drinking-water, background document for development of WHO guidelines for drinking-water quality”; World Health Organization, 2011.
3. V. Coman, B. Robotin, P. Ilea; *Resources, Conservation and Recycling*, 2013, *73*, 229-238.

Analysis of the Products and Wastes of a Pyrolysis Plant Powered by Residual Plastic Materials for Energy's Production

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Alternative and renewable energy sources are going to play an increasingly strategic role in the global landscape. Among them, the waste of plastic materials produced by our society are remarkable, establishing a potential renewable source for excellence. However, it's known that recovery and recycling technologies of waste are very often expensive. When these technologies aren't workable or economically convenient, it's useful to regain the energy in the so-called "quaternary recycling", using the plastic materials as alternative fuel. In fact, the average HHV of a mixture of plastics is about 35 MJ/kg. Actually, waste of plastic materials coming from automotive industry are transferred to landfills or to incinerators, but it should evaluate the high risk of formation of oxygenated heterocyclic compounds (e.g. dioxins) as well as of all the polluting substances (e.g. polycyclic aromatic hydrocarbons) during the combustion process. Taking into account these compounds, the research has been pointed on pyrolysis equipment where a syngas is formed in an oxygen-free environment with very low emissions from the plant in the atmosphere during the process. In collaboration with MECTRA s. r. l., equipped with an innovative pyrolysis plant, it was possible to propose an analysis of its products and by-products, in order to respect its good working and to achieve a minor environmental impact according to the limits of law. Synthetically, the process allows plastic materials coming from automotive industry to be transformed into combustible gas through a slow pyrolysis at temperatures between 400 to 700 °C. Thanks to a heating induction's system, the frequency can be calibrated according to the raw material chosen. At the end of the process, a gas with high HHV is produced and used to generate electricity by an alternator linked to an endothermic engine. The aim of the research, therefore, is the physical-chemical characterization of the input materials, the syngas produced, the emission fumes from the engine, the by-products formed during the process such as carbon black, ashes, hydrocarbons in both liquid and bituminous form, and washing waters. Concerning the parameters to be monitored on input materials, it is chosen to analyze ashes, HHV, moisture content, volatile heavy metals and the presence of sulfur and chlorine. Regarding the syngas, the analysis is focused in particular on the amount of methane gas, of higher volatile hydrocarbons and eventually of HCl and CO. About the emission of pollutants from the engine the study is mainly directed to the presence of toxic compounds such as dioxins and PAHs, in order to test the actual environmental impact eventually due to the choice of raw material. In the end, the analysis of by-products is based to understand their possible toxicity and their possible reuse, analyzing the presence of numerous metals and compounds such as PAHs and PCBs. In conclusion, the analytical characterization of the above mentioned parameters is particularly important, in order to verify the versatility of the pyrolysis process in its industrial application. This characterization, in addiction, could be a starting point of future legislative measures on the environment and on the potential of residual plastics as a renewable energy resource. For future perspectives, during the testing phase, the plant is going to be fed with biomass, such as rice straw, walnut shell etc., with electrical cables, composite packaging and tire coverings.

Sito di Monitoraggio in Alta Quota nelle Dolomiti Bellunesi (Col Margherita): Sistema Informatico per la Gestione Automatizzata dei Dati Meteo-Climatici.

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L'Istituto per la Dinamica dei Processi Ambientali (IDPA) del CNR gestisce un sito di misura di alta quota (Hight Altitude Station - HAS) in un'area remota a Col Margherita. La stazione di monitoraggio, accessibile dal passo San Pellegrino e dal passo Valles, situata nelle Dolomiti bellunesi a 2530 m sul livello del mare (latitudine 46° 22' 2.11" N, longitudine 11° 48' 23.03" E), è stata installata nell'estate del 2012 nell'ambito del progetto EU - FP7 Global Mercury Observation System (GMOS).

Per risolvere le problematiche legate alla gestione a distanza degli strumenti si è resa necessaria l'adozione di specifiche tecnologie hardware-software (IT) per l'acquisizione, gestione, trasmissione e validazione dei dati forniti dalla strumentazione automatica in dotazione alla cabina. Il sistema IT è stato progettato e sviluppato per permettere il controllo degli strumenti di misura di parametri chimico-fisici, della sensoristica meteo - climatica, delle telecamere interne/esterne della stazione.

Sviluppato su architettura Gnu-Linux, è stato utilizzato principalmente software Open Source. Sono stati integrati protocolli di comunicazione seriale per il controllo degli strumenti. L'acquisizione e la validazione dei dati viene gestita con LabView e Python. La sincronizzazione e il backup sono gestiti con Bash, crontab, scp e rsync. L'analisi statistica, la visualizzazione dei dati e la reportistica automatica sfruttano gli strumenti R, Shiny, Sweave e Latex.

Sono state considerate differenti soluzioni per la conservazione dei dati in rete (Cloud Storage) e per rendere fruibili i dati ad altri gruppi di ricerca, in accordo con gli standard Open Geospatial Consortium (OGC).

Attualmente il sito di misura è dotato di strumentazione meteo - climatica, di un analizzatore di mercurio atmosferico (TGM) e di ozono ed è in grado di integrare ai dati raccolti in automatico le misure di parametri chimico fisici ottenuti da campagne di monitoraggio hot-spot (inquinanti organici e inorganici nelle deposizioni atmosferiche, particolato atmosferico e neve).

L'obiettivo è realizzare la completa automazione dei processi di acquisizione, trasmissione, visualizzazione, validazione e produzione di report automatici dei dati misurati.

Adsorption of Triazine Herbicides on Carbon Nanotube Sponges

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Because of their exceptional surface area combined with excellent chemical, mechanical and thermal stability, materials based on carbon nanotubes (CNTs) are promising candidates for the extraction of organic substances from liquid media, either apolar compounds, in the native form, or polar compounds, after CNT functionalization. The adsorption ability of CNTs has been widely investigated in solid phase extraction of solutes from aqueous or non-aqueous matrices, aimed at concentration and/or isolation of the target analytes before chromatographic analyses[1]. Several comparative studies have revealed that adsorption ability of CNTs towards environmental pollutants is similar or higher than that provided by conventional silica-based sorbents or macroporous resins. While solid phase extraction based on packed columns or filters are suitable to treat relatively small volumes of aqueous samples, large-scale decontamination processes requires dispersion of the micrometer- or sub-micrometer-sized sorbent in the contaminated water. In this condition, the disadvantages related with high back-pressure and decrease of the real surface area typical of packed columns are eliminated, but recovery of the sorbent by filtration or centrifugation is necessary to permit its successive re-utilization. CNT sponges are bulk materials consisting of self-assembled interconnected CNT skeletons with high porosity which make them promising candidates for environmental applications such as sorption, filtration and separation[2]. In this investigation, some triazine herbicides have been identified as molecular probes to test the absorption efficiency of CNT sponges towards water organic contaminants. Symetric triazines (s-triazines) have been extensively used worldwide as herbicides to control unwanted plants in agriculture and in urban areas. Because of massive use and persistence in the soils, contamination of surface and ground water by triazine herbicides and their metabolites is an emergent environmental problem in intensively cultivated areas[3]. Due to their toxicity, triazine herbicides have been included in the list of priority pesticides and carcinogenic and endocrine-disrupting activity of specific compounds have been demonstrated. Apart from their environmental and toxicological relevance, our attention was focused on triazines because their properties (solubility in water, idrophilicity/idrophobicity, and partition between organic and aqueous media) can be largely modulated by moderate changes in the substitution pattern of the triazine skeleton. In particular, the substituent pattern can influence the polarizability of π-electrons of the aromatic triazine ring and govern the efficiency of π-π interactions, regarded as the main intermolecular forces responsible for absorption on CNTs. In addition, other kinds of non-covalent intermolecular forces, such as dipolar interactions and hydrogen bonding are influenced by the degree of alkylation of the amino groups.

References

1. Socas-Rodríguez et *al*.; "Recent applications of carbon nanotube sorbents in analytical chemistry"; *J. Chromatogr. A*, 2014, 1357, 110-146.
2. Gui et *al*.; "Carbon nanotube sponges"; *Adv. Mat.*, 2010, *22*, 617-621.
3. Sabik et *al*.; "Multiresidue methods using solid-phase extraction techniques for monitoring priority pesticides, including triazines and degradation products, in ground and surface waters"; J. Chromatogr. A, 2000, 85, 217–236.

Determination of Pesticides in Baby Food by Means of MEPS Followed by UHPLC-MS/MS Analysis

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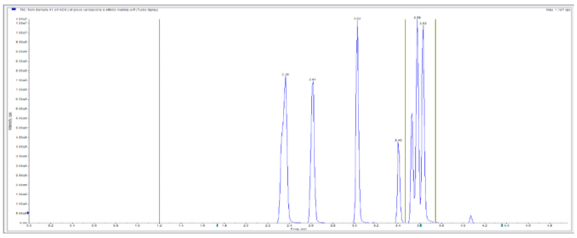
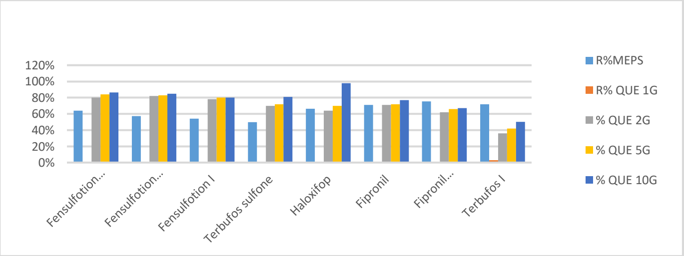
Processed cereal-based baby food is an essential nutritional source for infants and young children, which are vulnerable for their poor immunologic system and low weight[1]. To protect their health the European Union Baby Food Directive 2006/141/EC designed pesticides as prohibited, and in some case their residue has a maximum residue limit /MRL) set between 3-8 µg/kg [2]. In the last years, in pesticides residue analysis, QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) developed by Anastassides et *al.*[3] is the most common extraction procedure of pesticides from cereal and cereal based sample. In this work a method for the analysis of pesticides with the lowest MRLs (3-4 µg/kg) in baby food based on MEPS clean-up has been developed, also comparing MEPS with QuEChERS. Two hundred mg of sample were extracted with acetonitrile-acetate buffer (60:40 v/v); the mixture was sonicated and centrifuged for 5 min at 10,000 rpm at 20°C. An aliquot of supernatant was then subjected to the clean-up procedure using MEPS with highly cross-linked polystyrene divinylbenzene (HDVB) stationary phase. The chromatographic analysis was performed by an UHPLC coupled with triple quadrupole mass spectrometer. The acquisition window was split in three periods and quantitative analysis was carried in Multi Reaction Monitoring (MRM), selecting two precursor ion/fragment ion transitions for each analyte.





The best condition to extract all the analytes were studied: organic phase, amount of sample and extracting volume and stationary phase. After that QuEChERS was compared to our MEPS extraction procedures and we have demonstrated that we obtain better recovery an even a great enrichment factor, a reduction of time, amount of sample and organic solvent. Finally, the proposed method was validated according to SANCO/12571/2013 document: the validation data proved satisfactory reproducibility and accuracy demostrating the method is well suited to detect all analytes. In conclusion, the presented research allowed us to develop a method for the determination of several pesticides and their metabolites in baby-food at very low concentration values.

References

1. Sherif S.O., Salama E.E., Abdel-Wahhab M.A. Mycotoxins and child health: The need for health risk assessment. Int J Hyg Environ Health. (2009) 212(4), 347–68.
2. Commission Directive 2006/141/EC of 22 December 2006 on infant formulae and follow-on formulae and amending Directive 1999/21/EC. Off. J. Eur. Union, L 401 (2) 30.12.2006.
3. Anastassiades M.L., Lehotay S.J.M., Stajnbaher D., Schenck F.J. Fast and easy multiresidue method employing acetonitrile extraction/ partitioning and B dispersive solid-phase extraction for the determination of pesticide residues in produce. J AOAC (2003) 86, 412–31.

Evaluation of the Presence of Inorganic and Organic Contaminants in Soils and Vegetables Cultivated in Urban Gardens

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In recent years, urban horticulture has had a great expansion; the principal reasons are to be sought in the possibility to produce fresh and low-cost vegetables and reduce environmental and socio-economic problems[1,2,3]. These reasons induce many cities in the world to assign common green areas to the citizens for urban horticulture. Turin is one of the Italian cities having many urban gardens thanks to "TOCC – Città da coltivare" project[4]. In order to re-evaluate abandoned green areas municipalities entrust urban lands to citizens willing to cultivate them. Nevertheless, since these areas are collocated within urban centers, both soils and vegetables grown therein are subjected to continuous pollution sources such as vehicular traffic, atmospheric pollution and contaminated irrigation waters. Moreover, the presence of both civil and industrial buildings could determine the contamination of the soil and hence the vegetables there cultivated by root uptake. The intake of vegetables contaminated by organic and/or inorganic pollutants can have serious risks for human health. For these reasons, sometimes the benefits, derived from vegetables cultivated in urban gardens, are questioned[5], and therefore urban horticulture requires further and careful studies. In this context, the aim of our study is to obtain an overview of pollution levels present in nine urban gardens, localized in Turin and in its neighboring, to understand how the anthropic activities can adversely affect these areas. For this purpose, we have determined inorganic and organic pollutants content in both soils samples and vegetables collected in these urban gardens. The elemental concentrations in soils and vegetables were determined by ICP-AES, GF-AAS and SF-ICP-MS whereas organic pollutants were analyzed by GC-MS. High concentrations of chromium and nickel have been found both in soils and in vegetables: the presence of these elements can be due to anthropic sources or, most likely, to the litogenesis of this area derived from Cr-Ni-serpentinites. This study has evidenced that the absorption capacity of heavy metals in soil depends strongly from considered plant species: lettuce and rosemary, for example, have lower concentrations of various heavy metals than the other considered vegetables (cabbage, sage, tomatoes leaves, etc.) even if they are cultivated in the same site. Indeed, we have found similar metal concentrations for the same plant species cultivated also in different urban gardens. Regarding organic pollutants, the presence of some polycyclic aromatic hydrocarbons (PAHs) was observed in the soils and in the vegetables, arising primarily from the incomplete combustion of organic materials of anthropic activities. The multivariate elaboration of experimental data has confirmed a clear difference among several plant species with regard to their inorganic and organic composition. By way of conclusion, we can suppose that in urban gardens is preferable to cultivate only specific plant species less affected by possible pollution of the area, such as, for example, lettuce and rosemary.

References
1. FAO (Food and Agriculture Organization of the United Nations), Urban agriculture and food security, 2010.
2. Waliczek T.M., Zajicek J.M., Lineberger R.D. *Hortscience*, 2005, *40*, 1360–1365.
3. Brown K.H., Jameton A.L. *J. Public Health Policy*, 2000, *21*, 20–39.
4. www.ortiurbanitorino.it., 2015.
5. Sämuel I., Kotsyuk I., Hölscher M., Lenkereit C., Weber F., Kowarik I. *Environmental Pollution*, 2012, *165*, 124–132.

Elemental Carbon, Primary and Secondary Organic Carbon in a Coastal Site in South Italy

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Carbonaceous PM is composed of a refractory component, commonly called elemental carbon (EC), and an organic fraction, called organic carbon (OC). Organic aerosols represent a large fraction of atmospheric aerosols. The organic fraction can include saturated and unsaturated aliphatic compounds, aromatic compounds, alcohols, ketones, aldehydes, carboxylic acids, amines, sugars, polyols, and organic sulfur compounds[1,2]. Organic and elemental carbon were measured in daily PM10 and PM2.5 and 6 hours range time PM2.5 samples collected from September 2015 to October 2015 in a coastal rural site near Brindisi in the Apulia region (Italy), in order to determine factors affecting the carbonaceous aerosol variations. OC and EC were measured on Sunset Laboratory Thermal–Optical Carbon Aerosol analyser using NIOSH protocol. Carbon content (total carbon TC) represented a considerable fraction for both PM10 and PM2.5. The highest values for both parameters were recorded when the winds blows from NE Europe and when Sharan Dust events have been recognized. The results show that OC and EC exhibited higher concentrations during the night hours, suggesting that stable atmosphere and lower mixing play important roles for the accumulation of air pollutants and hasten condensation or adsorption of volatile organic compounds. Moreover, ATR-FTIR analysis were performed on some samples with the lowest and the highest OCsec and on samples characterized by Saharan Dust event. FTIR spectroscopy provides absorption peaks which can be identified and assigned to chemical bonds to identify functional groups in a complex sistem. The FTIR method is relatively simple and rapid and requires only small sample size. To our knowledge, there are only few examples of recent studies which are subjected to quantification or qualification of chemical species of aerosol samples. FTIR coupled with attenuated total reflectance (ATR) is a new technique developed recently. ATR FTIR analysis were carried out and it let identify organic functional groups included non-acid organic hydroxyl C-OH group (including sugars, anhydrosugars, and polyols, herein indicated as alcohol group), aromatic C=C-H group, aliphatic unsaturated C=C-H group, aliphatic saturated C-C-H group, non-acid carbonyl C=O group, carboxylic acid COOH group, and amine NH2 group. Among the inorganic ions, carbonates, sulfate, silicate and ammonium can be recognized.

References
1. Genga A., Ielpo P., Siciliano M., Siciliano T.; “Carbonaceous particles and aerosol mass closure in PM2.5 collected in a port city”; *Atmospheric Research*, 2017, *183*, 245-254.
2. Gilardoni S., Liu, S. Takahama, S. M. Russell, L. Allan, J.D. Steinbrecher, R. Jimenez, J. L. De Carlo, P.F. Dunlea E.J., Baumgardner D.; “Characterization of organic ambient aerosol during MIRAGE 2006 on three platforms”; *Atmos. Chem. Phys.*, 2009, *9*, 5417–5432.

Study of Endocrine Disrupting Compound Release from Medical Devices in Plasma Samples of Premature Newborns Through an On-line SPE UHPLC-MS/MS Method

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Endocrine disrupting compounds (EDCs) are exogenous substances that mimic and antagonize the effect of endogenous hormones. EDCs may interfere and influence the human development disrupting the synthesis and the metabolism of hormones and of their receptors[1]. Furthermore, the effects of these chemicals are not only limited to the adult life but they can also be passed on to future generations by the probable mechanism of transgenerational epigenetics inheritance[2]. Differently from adults, infants are not exposed only to chemical toxicants in the environment but they may be also exposed to EDCs indirectly during their intrauterine life. EDCs generally tend to be highly lipophilic and they can easily accumulate in fat stores inside the body. Hence, the underdeveloped reproductive apparatus and immune system during fetal and post-natal life can be exposed to unusually high concentrations of compounds that cannot be easily metabolized or excreted at these stages of development[3]. In addition, some studies reported a possible correlation between chemical exposures to EDCs of the mothers and pregnancy preterm. This study deals with the development and validation of a new analytical method for the determination of 21 selected EDCs belonging to different chemical classes (5 parabens, 2 bisphenols, 2 alkylphenols, 1 antibacterial soap, and 11 perfluorochemicals) in plasma samples. The aim was to analyze these compounds in blood samples of premature newborn patients of the Neonatology Department of Ospedale Maggiore of Novara. The analyses were carried out by UHPLC-MS/MS. The plasma samples were subjected only to protein precipitation with cold acetonitrile, centrifuged and diluted 1/10 (v/v) before purification and pre-concentration through an on-line SPE system (loading at flow-rate 3.0 mL/min for 2 min) directly interfaced with the UHPLC-MS/MS. Different SPE cartridges and chromatographic columns were tested, in order to obtain the best conditions with respect to the analytes separation, the pre-concentration factors, LODs and LOQs, injection volume and system backpressure. Starting from 200.0 μL of plasma, the LODs of the method range from 0.1 pg/mL for perfluorobutyl sulfonate to 14.9 pg/mL for bisphenol A, the recovery values being always greater than 85% and the total run time less than 9 min. The first step of the study was to identify a possible release of EDCs from the medical devices and successively the EDC accumulation in plasma of the newborns during the therapies to which infants have been subjected. Premature infants need in fact intensive medical care and they must be nourished only with parenteral solutions by tubes, intravenous catheters, and other medical devices for almost 2-3 months. Simulation of leaching on the syringes and the butterfly were carried out by using physiological solutions (3 solutions from different manufacturer) for the same contact time of the blood draws. As concerns the catheters, the simulations of release were carried out outside with the physiological solution and inside with the parenteral one for 2 week of contact time, equal to the time of permanence of the catheter into the infant body. The results show the presence of some EDCs both in physiological solution and in the medical devices commonly used during the infant hospitalization. The study is still ongoing and other plasma samples will be collected.

References
1. S. Shekhar, S. Sood, S. Showkat, C. Lite, A. Chandrasekhar, M. Vairamani, S. Barathi, W. Santhosh; *Gen. Comp. Endocrinol.*, 2017, *241*, 100-107.
2. M.K. Skinner, M. Manikkam, C. Guerrero-Bosagna; *Reprod. Toxicol.*, 2011, *31*, 337-343.
3- T.T. Schug, A. Janesick, B. Blumberg, J.J. Heindel, 2011, *127*, 204-215.

Microbusters, an integrated approach for the treatment of micropollutants: the key role of suitable analytical tools

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The "Microbusters" project, funded by Compagnia di San Paolo and University of Torino, aims to develop an innovative integrated tertiary water treatment for the removal of micropollutants (MPs) such as pharmaceuticals, personal care products, etc…., from natural as well as treated waters. Wastewater treatment plants are not specifically designed nor optimized for MPs abatement at trace concentrations (from few ng/L to several μg/L). Thus, many of these MPs are still present at the end of wastewater treatment processes and can re-enter the water cycle. The presence of MPs in natural waters has been associated with many negative effects, such as short- and long- term toxicity, endocrine-disrupting effects, antibiotic resistance of microorganisms. Microbusters deals with the development of novel materials for optimizing four complementary technologies that have shown promising results in the treatment of MPs, namely membranes, adsorption, biocatalysis and photocatalysis. Moreover, based on the preliminary results, the present research has the ambitious goal of creating a consortium of academic and industrial partners for preparing a proposal under H2020, including the Life Cycle Assessment of new materials and the design of a prototype for MPs abatement in real waters at pilot plant scale. To face these aspects, beside additional expertise in the field of biology, engineering, economics, environmental and soil chemistry, the development of suitable analytical tools for MPs analysis at sub-trace level is mandatory. A list of 16 MPs, chosen on the basis of their presence in surface waters and toxicological interest, has been considered for the development of fast and sensitive UHPLC-MS/MS methods. Since the physical-chemical properties of the chosen analytes range from the high polarity of glyphosate and its degradation product AMPA to the more lipophilic alpha-cypermetrin and nonylphenol, three different analytical methods have been developed. Glyphosate and AMPA have been separated by an HILIC-MS/MS method, whereas the other two methods consist in the separation on an Eclipse XDB-C18 column (4.6x50 mm 1.8 μm, Agilent) of eight basic species (caffeine, carbamazepine, tricyclazole, diclofenac, acetaminophen, terbuthylazine, tetracycline, amoxicillin) that ionize in positive ion mode, and of five acidic species (nonylphenol, bisphenol A, butylparaben, triclosan, clofibric acid) that easily ionize in negative ion mode. All the UHPLC-MS/MS methods have been directly interfaced with on-line SPE, not only to purify the water samples, but also to pre-concentrate the MPs on the SPE HLB cartridge (2.1x20 mm, 25 μm, Waters) that is able to retain all the analytes thanks to its versatility. The analytes have been loaded on the SPE cartridge for 2 minutes at flow-rate of 2.0 mL/min in order to achieve LOD and LOQ values of the order of few ng/L. All the methods have been validated according to the UNI CEI EN ISO/IEC 17025, evaluating LODs, LOQs, linearity range, sensitivity, reproducibility, selectivity, accuracy, recovery, and matrix effect. The obtained recovery values are greater than 94%, whereas the absence of matrix effect is the result of the optimized washing step of SPE sorbent, which employs a washing volume of about 30-folds the column volume. These analytical procedures will be applied to different water samples (surface river waters, groundwater, samples taken at different stages in a water treatment plant) before and after spiking with a known amount of the 16 MPs, in order i) to perform a screening of their presence and concentration level; ii) assess the matrix effect on their determination. Afterwards the analytical procedures will be applied to evaluate the efficiency of the above-mentioned tertiary water treatments for MPs removal.

Development of Two Colorimetric Assays For Real Time Monitoring Of Saxitosin In Sea Water

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Saxitoxin (STX) is one of the most lethal non-protein toxins (LD_{50} = 9 µg Kg^{-1}) and is the only marine natural product that has been declared chemical weapon. STX has the ability to bio-accumulate up trophic levels. Ingestion of infected marine organisms, by humans, induces a lethal disease known as Paralytic Shellfish Poisoning (PSP) that is currently without antidote or detoxification pathway. The maximum tolerance levels, as established by the European Union and according with the Food and Drug Administration, refer to 40 - 80 µg PSP x 100 g edible portion of fresh, frozen or tinned shellfish. The goal of this work is to develop rapid tools for monitoring the presence of STX in sea water. Two methods are proposed: a flow injection immunoassay system (FI-IA) and an Enzyme-Linked Immuno-Magnetic Colorimetric assay (ELIMC), both based on colorimetric detection.

The first method (FI-IA) consists in an off-line incubation of the sample containing STX with fixed amounts of anti-STX antibody and STX labelled with HRP until the equilibrium is established. The mixture is then injected into a flow system where the separation of the free Ag* and the antibody-bound tracer is performed in a column with immobilized protein G. In the column, all the antibodies are retained due to the protein G affinity for the constant fragment of the antibody.

The second assay is a direct competitive ELIMC where free STX and STX- HRP labeled (STX-HRP conjugate) compete towards the anti-saxitoxin antibody immobilized on the surface of magnetic beads (MBs), pre-coated with IgG anti-mouse. Separation of the unbound conjugate and the unbound free STX it is performed by capturing the MBs with a magnet and discarding the supernatant. The activity of the enzyme labelled STX is measured spectrofotometrically using the TMB+H_2O_2 as substrate. The optimized immune-analytical system was compared to a commercially available STX-ELISA kit.

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Determination of Hydrocarbons C >12 In Soil Samples

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Hydrocarbons monitoring plays a key role to evaluate the soil quality in urbanized areas, in particular, where are present oil pumps or industrial facilities and residential areas. In recent years, the environmental concern on soils potentially contaminated by heavy hydrocarbons has increased; the current legislation focuses its attention on residential areas nearby highways or exposed to high vehicular traffic, establishing a limit value of 50 mg/Kg of total hydrocarbons. In this framework, the ISO16703:2011 method suggests to determine total hydrocarbons by GC-FID. Our study aims to optimize the proposed method in order to find the best analytical conditions to quantify hydrocarbons C>12 in soil samples. Several soil samples were collected in residential areas and close to industrial sites. Before analysis by GC-FID soil samples were spiked with different concentrations of hydrocarbons, ranging between 15 mg/kg to 75 mg/kg, and Tetracontane was added to each sample as internal standard. In order to evaluate the influence of the matrix effect on the extraction efficiency, the internal standard was added in the extraction solvent, as suggested by ISO16703:2011, or directly on the soil samples. Results from the second approach indicated a better reliability. Repeatability and other quality control parameters were investigated, confirming the good performance of the chosen method. Heavy hydrocarbons (C12-C40) were present in all samples, but samples collected close industrial areas showed an unresolved complex mixture (UCM) in the gas-chromatograms, evidence of potential oil spills.

Target and Not-target approach for the identification of pesticides and emerging contaminants in paddy water

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Rice crop requires a great amount of chemicals like fertilizers and pesticides. Nowadays, pesticides formulations are designed to offer both high selectivity and low persistence in the environment and they can undergo degradation by the effect of the environmental conditions as water, sunlight and bacteria.

According to previous studies, pesticides can potentially transform into new emerging contaminants, more toxic than the precursors[1-4], by the effect of sunlight or other environmental factors.

In this study, paddy water samples collected a rice farm located in the main Italian rice basin (north-western zone of the Padana Plain) in the North-Western zone of Italy were analyzed by the use of a micro LC system interfaced with a quadrupole-time of flight (QTOF) high resolution mass spectrometer. The quality of water was therefore evaluated according to two approaches: target and non-target.

Using the target approach, the most used pesticides in rice cultivation (like Imazamox, Oxadiazon, Pendimethalin, Profoxydim and Tryciclazol) were identified and quantified.

Regarding the non-target approach, since the well-known difficulties associated to structure elucidation and the limited availability of mass spectral libraries for LC-HiresMS, all the mass and mass/mass spectra were recorded using the SWATH^{TM} (Sequential Window Acquisition of all THeoretical Mass Spectra) acquisition method. In this way, the presence of new emerging contaminants, originated from the degradation of the pesticides was investigated and their probable chemical structures were elucidated.

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References
1. M. Bottaro, P. Frascarolo, F. Gosetti, E. Mazzucco, V. Gianotti, S. Polati, E. Pollici, L. Piacentini, G. Pavese, M.C. Gennaro, J Am Soc Mass Spectrom 19 (2008) 1221–1229.
2. F. Gosetti, M. Bottaro, V. Gianotti, E. Mazzucco, P. Frascarolo, D. Zampieri, C. Oliveri, A. Viarengo, M.C. Gennaro, Environ Pollut 58 (2010) 592–598.
3. F. Gosetti, U. Chiuminatto, D. Zampieri, E. Mazzucco, E. Marengo, M.C. Gennaro, J Chromatogr A 1217 (2010) 3427–3434.
4. F. Gosetti, U. Chiuminatto, E. Mazzucco, R. Mastroianni, B. Bolfi, E. Marengo, Environ Sci Pollut Res, 22 (2015) 8288–8295.

Imazamox Loads In Irrigation Tailwaters And Percolation Fluxes From Paddy Fields In Northern Italy

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Italy is the Europe leading rice producer, with more than half of the total production and a high quality level. Although the main function of paddy areas is the production of rice, these complex agro-eco-systems are linked to issues of great concern such as the freshwater conservation in terms of both water consumption and water quality. An intensive experimental activity was started in 2015, in the framework of the WATPAD project (Fondazione Cariplo, Grant No 2014-1260), to investigate the water balance terms and the water quality impacts on surface water and groundwater of four paddy fields located in Lomellina (western part of the Po river plain). A different irrigation management was adopted for the four paddies: wet seeding and continuous flooding (WFL) was applied within two fields, while dry-seeding and delayed flooding was adopted for the other two paddies. The four fields were instrumented with devices measuring irrigation inflows and outflows, water level in the fields, soil moisture and groundwater depths. Additionally, in each field, three couples of porous cups were installed at depths of 25 and 60 cm. Water samples of irrigation inflows and outflows, water in porous cups, and groundwater were collected along the agricultural season (26 sampling dates in 2015). Water samples were analyzed for various compounds, including the herbicide Imazamox and its degradation products. The contemporaneous quantification of water fluxes and Imazamox concentrations allowed the determination of Imazamox loads released in surface waters and groundwater along the agricultural season for each field. The main findings, which will be discussed in the poster, are the following: *i)* most of the Imazamox loads leave the paddies through percolation; consequently, fields characterized by more permeable soils contribute more to Imazamox concentrations in groundwater; *ii)* Imazamox loads in surface outflows are modest, as the half-life of Imazamox in surface waters reached by solar radiation is very low[1]; *iii)* from the data available to date (agricultural season 2015) Imazamox concentrations in porous cups may seem to be influenced from the concomitant use of fertilizer products. In particular, it is known from the literature that the degradation of Imazamox is pH and oxygen dependent[2,3]; thus, the use of fertilizers having an effect on these water parameters could influence the Imazamox persistence in the field, favoring its transport to groundwater; *iv)* more research is needed to investigate the eventual field interaction between Imazamox and the use of fertilizers, as well as to monitor the environmental fate of Imazamox degradation products.

References
1. E. Quivet, R. Faure, J. Georges, J.O. Paissé, B. Herbreteau, P. Lantéri, J Agric Food Chem, 54 (2006) 3641-3645.
2. T.M. Aichele, D. Penner, Weed Technol, 19 (2005) 154-159.
3. M. Milan, A. Ferrero, S. Fogliatto, F. De Palo, F. Vidotto, J Agr Sci-Cambridge (2016) 1-13.

Rapid PAH Determination in Beer Samples by DLLME-GC-IT/MS Protocol

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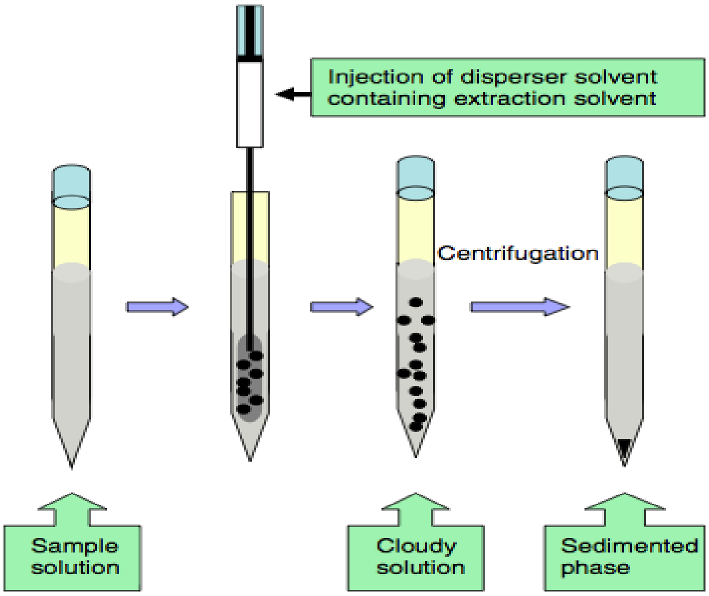
Beer is the world's most widely consumed alcoholic beverage, and is the third-most popular drink overall, after water and tea. It is thought by some to be the oldest fermented beverage. The process of making beer is known as brewing. About the main composition, beer contains phenolic acids, 4-hydroxyphenylacetic acid, vanillic acid, caffeic acid, syringic acid, p-coumaric acid, ferulic acid and sinapic acid whereas among environmental contaminants, the Polycyclic Aromatic Hydrocarbons (PAHs) are recognized as a global problem due to their chemical stability and carcinogenic effects. An Ultrasound-Vortex-Assisted Dispersive Liquid-Liquid Micro-Extraction (USVADLLME) procedure (the main steps of the procedures are reported below) coupled with a Gas Chromatography-Ion Trap Mass Spectrometry (GC-IT/MS) is proposed for fast analysis of nine Polycyclic Aromatic Hydrocarbons (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, crysene, benzo(b)fluoranthene, benzo(a)pyrene and benzoperylene) in beer (alcohol by volume ≤ 7 %). Among 5 possible extraction solvents tested, dichloromethane (density 1.325 g mL^{-1} at 25 °C) was selected for further method development. Parameters such as extraction solvent type and volume, extraction time and pH, and NaCl concentration were optimized. Under optimal conditions, the enrichment factor of the nine analytes ranges between 100 and 1000 fold and the recoveries from 83 % to 99 % and correlation coefficients range from 0.998 to 0.999. The limit of detection (LOD) and limit of quantification (LOQ) are ≥ 3.8 pg μL^{-1} and ≥ 9.8 pg μL^{-1}, respectively. The precisions expressed as relative standard deviation (RSD), are ≤ 4.0 %. The entire methodology has been applied to 11 real samples (9 commercial beer samples packed by bottle and tin, and 2 special commercial beers), available in the Italian market. The only PAH present in all the samples is the chrysene, which is not relevant from a human health point of view. On the other hand, a systematic PAH presence in the samples has not been found: the only interesting issue regards the benzo(a)pyrene level in two samples. Even if it is not possible to identify the source (this should be just possible analyzing the raw materials of these two beer samples), this analysis confirms the importance of having a fast, valuable and reliable protocol for analyzing such compounds.



Analytical Methods to Study the Fate of Carbon in Soil Treated with Biochar

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Biochar is the carbonaceous solid obtained from pyrolysis of biomass. The addition of biochar to soils can improve fertility, meanwhile mitigating climate changes by sequestering organic carbon into a form resistant to mineralization. The porous carbonaceous structure of biochar can reduce the mobility of contaminants and improve removal efficiency due its sorptive capacity. These last properties are of particularly interest in riparian zones. However, after application, biochar is subjected to different factors that can alter its performance, like physical (vertical transport, horizontal and lateral export, slacking), biological and chemical processes. Oxidation is known to favours the degradation of the otherwise highly recalcitrant aromatic ring structures. Moreover, biochar affects the properties of soil organic matter by contributing with labile and stable polyaromatic structures[1], releasing humic-like components[2], influencing the aggregates and the soil microbial community structure. In order to understand the fate of carbon in the soil it is important to have suitable analytical tools that are not affected by the recalcitrance of the biochar. The capacity of the technique to discriminate between labile soil and stable biochar fractions is a valuable characteristic. HyPy, analytical pyrolysis in the presence of hydrogen, has been recently used to this purpose[1]. In this study, we have tested different techniques to characterise the organic carbon in reference soils treated with biochar. The biochar samples were obtained from different biomass and pyrolysis conditions, and included a biochar from a model up-draft gasifier utilised in riparian zones in field experiments. The content of inorganic and organic elemental carbon in the model soil/biochar systems was investigated by TOC analyser and CHN elemental analyser. Both techniques utilize catalyzed combustion detecting generated CO_2 by IR or TCD. Thermogravimetric analysis (TGA) was utilised to evaluate the possibility to discriminate labile (humic fraction) and stable (biochar) carbon components. The volatile matter released by TGA was characterised by analytical pyrolysis (Py-GC-MS) in order to individuate potential molecular markers of the various organic fractions of the treated soils (humic matter, biochar, sewage sludge, etc.). The preliminary results obtained from these soil model systems enabled highlighting the limits and advantages of the different techniques. TOC and CHN provided similar values with experimental variability confirming that these techniques are adequate to investigate the dynamic of carbon in soil treated with biochar. Molecular ratios (e.g. toluene/naphthalene/methylnaphthalene) from Py-GC-MS can be used to discriminate different biochar types, but failed as markers in soils for biochar with relatively low H/C ratios. Data from TGA were affected by experimental conditions and the presence of carbonates, but important information can be obtained. Acknowledgments: Study conducted within the project "Uso del biochar come filtro biologico" PSR misura 16 Focus Area 4B Regione Emilia Romagna. Sauber srl and Super Taurus srl, Az. Sperimentale Vittorio Tadini, Az. Agraria Sperimentale Stuard S.c.r.l. were acknowledged for the biochar and soil samples and helpful discussion.

References
1. A.G. Rombolà, W. Meredith, C.E. Snape, S. Baronti, L. Genesio, F.P. Vaccari, F. Miglietta, D. Fabbri, *Environ. Sci. Technol.*, 2015, 49,11037–11044.
2. M. Ghidotti, D. Fabbri, O. Masek, C. L. Mackay, M. Montalti, A. Hornung, *Environ. Sci. Technol.*, 2017, DOI: 10.1021/acs.est.7b00520.

Major and Trace Elements in The Aerosol Of Central Antarctica, Dome C (Italo-French Station "Concordia")

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Major and trace elements (Al, As, Ca, Cd, Co, Cu, Fe, La, Mg, Mn, Mo, Na Ni, Pb, Ti, Zn) were determined for the first time in the aerosol collected at Dome C, Concordia Station, in the Antarctic Plateau. PM10 samples were collected during summer 2005-2006 using three high-volume samplers in two different locations: the first was very close to the station (about 50 m downwind), while the other was at the Astrophysic Tent (~800 m far upwind of the station), with two samplers installed very close to each other (sites called Astrophysic Tent 1 and 2) (1). The aims were: i) to investigate the direct impact of the station on aerosol metal concentrations and ii) to determine concentrations in a clean area, under the hypothesis of no effect of the station, according to the prevailing wind direction. The availability of the aerosol mass, which was directly measured in Antarctica by differential gravimetry, allowed us to express metal contents in terms of both mass fractions and atmospheric concentrations (1-4). Determinations were carried out by Square Wave Anodic Stripping Voltammetry (SWASV) (4) and by Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS) (5). Results, expressed in terms of atmospheric concentrations, showed that the major constituents (Na, Ca, Mg, Al, Fe) were present in the order of ~1 ng/m^3, while for trace elements values increased from a few units of pg/m^3 (Cd, Co, As, La), to a few tens of pg/m^3 (Pb, Mo, Ti), to hundreds of pg/m^3 (Cu, Mn, Ni, Zn). In general, the highest element concentrations (e.g. Cd, Pb, Cu, Zn and As) were observed around the beginning of the expedition, for each sampling site. This can be attributed to a general contamination of the area connected to the intense activity at Concordia station, including aircraft arrivals/departures. Conversely very low values were observed subsequently especially at the Astrophysic Tent. Interestingly, when in a few days of the intermediate period the wind direction reversed with respect to the prevailing direction (i.e. from the North instead of from the South), the metal concentrations, especially of Cd and Pb, decreased at Concordia and increased at Astrophysic Tent. Principal Component Analysis allowed us to recognize three groups of elements, which were associated to typical sources, as generally recognized in the area also from measurements in snow and ice. In particular Al, La and Ti appear mainly related to crustal origin; Na, Ca, Mg, Ni, Co, Mo and Fe seem all associated to the marine source; Pb, Cd, Cu, Zn, As may be referred to the anthropic source, mainly the local human presence and activity.

References

1. A. Annibaldi, C. Truzzi, S. Illuminati, G. Scarponi, Anal Chem 83 (2011) 143.
2. C. Truzzi, A. Annibaldi, S. Illuminati, C. Mantini, G. Scarponi, Air Qual Atmos Health (2017), doi: 10.1007/s11869-017-0470-3.
3. C. Truzzi, L. Lambertucci, S. Illuminati, A. Annibaldi, G. Scarponi, Ann Chim 95 (2005) 867.
4. S. Illuminati, A. Annibaldi, C. Truzzi, G. Libani, C. Mantini, G. Scarponi, J Electroanal Chem 755 (2015) 182.
5. M. Malandrino, M. Casazza, O. Abollino, C. Minero, V. Maurino, *Chemosphere* 147 (2016) 477.

Study of As^{3+} interaction with thiols in aqueous solution

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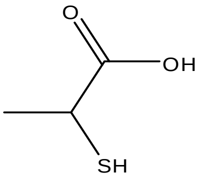
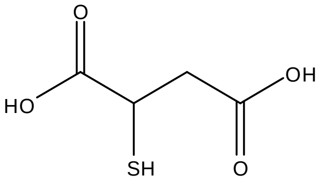
Arsenic is an ubiquitous element present in trace in all environmental compartments and in living organisms[1]. About 60% of the arsenic is released by natural sources, as volcanic activity, but it is also due to human activities, since As compounds have numerous applications, for example in the glass and semiconductor industries, in agriculture, as pesticides and herbicide, and in many other fields[2]. Accordingly, the environmental arsenic contamination represents one of the most important problem of environmental toxicology. Its toxicity, mobility and bioavailability depends on speciation, which represents the distribution of the element amongst defined chemical species in a system. Arsenic(III) compounds, for example, are more dangerous than those containing arsenic(V) owing to the high affinity for the proteins sulfhydryl groups. A possible bond with these proteins could alter their conformation and prevent the normal interaction with other functional proteins[3]. Despite the importance of As^{3+} interactions with sulfhydryl groups, very few thermodynamic studies are reported in literature. In light of this, an investigation on As^{3+}/S-donor ligand complexation was started in aqueous solution, with particular attention to physiological conditions. In this contribution, results obtained on As^{3+}-TLA and As^{3+}-TMA systems are reported.



2-mercaptopropanoic acid or thiolactic acid (*TLA*)



2-mercaptosuccinic acid or thiomalic acid (*TMA*)

Studies were performed by different analytical techniques, such as potentiometry and spectrophotometry UV/Vis, in order to define the speciation model and all thermodynamic parameters concerning the species in solution, together with ^{1}H NMR spectroscopy in order to gain information on coordination mode.

The best speciation models obtained for the As-TLA and As-TMA systems are featured by five species: ML, MLH, ML_2, ML_2H and ML_2H_3 for As-TLA and ML, MLH_2, MLH, M_2L and MLOH for As-TMA system. For each ligand, the sequestering ability towards As(III) was determined using an empiric parameter known as $pL_{0.5}$, that, numerically, represents the concentration of ligand required to sequester the 0.5 of metal fraction.

References
1. Mandal, B.K.; Suzuki, K.T. Arsenic round the world: a review. Talanta, 2002, 58, 201-235.
2. Leermakers, M.; Baeyens, W.; De Gieter, M.; Smedts, B.; Meert, C.; De Bisschop, H.C.; Morabito, R.; Quevauviller, Ph. Toxic arsenic compounds in environmental samples: Speciation and validation. Trends in Analytical Chemistry, 2006, Vol. 25, No. 1.
3. Shen, S.; Li X.F.; Cullen, W.R.; Weinfeld, M.; Le, X.Chris Arsenic Binding to Proteins. Chem Rev., 2013, 113, 7769−7792.
4. Crea F.; De Stefano C.; Foti C.; Milea D.; Sammartano S. Chelating agents for the sequestration of mercury(II) and monomethyl mercury(II). Curr. Med. Chem., 2014, 21, 3819-3836.

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Thermodynamic Study Of Naringin Under Physiological Conditions

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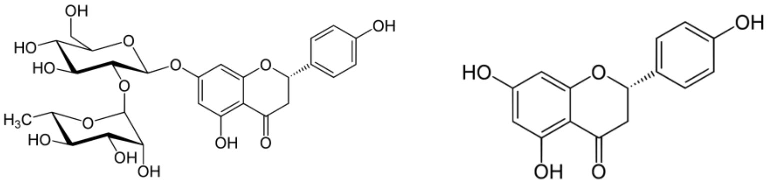
Naringin and its metabolite naringenine (Scheme 1 a and b, respectively) are antioxidants of many citrus fruits.



a b

Scheme 1: Structure of naringin (a) and naringenine (b).

Naringin is the largest flavonoid present in grapefruit and has anti-ulcer, anti-inflammatory and antioxidant activity. Naringenine inhibits breast cancer proliferation and delay the genesis of breast cancer. Due to their interesting properties, naringin and naringenine have attracted the interest of several scientists in recent years[1,2] .

The solubility evaluation of drugs plays an important role in the choice of the solvent suitable for the development of industrial production processes and pharmaceutical product design.

Solubility data are required to determine the most suitable solvents for extraction, separation, production and purification of organic compounds. The solubility of naringenine in the binary ethanol/water system has been reported in recent work[3]. However, comparative studies on the phenomenon of naringin and naringenine solubilities in different solvents are less studied and the information is therefore limited. Although they have a similar structure, naringin and naringenine may exhibit a substantial difference in their behavior in aqueous solution. Most real solutions show a non-ideal behaviour, so it is necessary to evaluate the effect of solvent on the analytes solubility (salting-in and salting-out). Knowledge of the analytic dissociation constants, too, may be useful for prediction of the optimal *in vivo* absorption site.

The aim of this work was to determine the solubility and the acidic constants of naringin in pure water and under physiological conditions (*i.e.* 0.16 M NaCl and 37°C).

References
1. L. Zhang, L. Song, P. Zhang, T. Liu, L. Zhou, G. Yang, R. Lin, J. Zhang, *J. Chem. Eng. Data*, 2015, *60*, 932.
2. C. Mielczarek, *Eur. J. Pharm. Sci.*, 2005, *25*, 273.
3. J. Zhang, P. Zhang, T. Liu, L. Zhou, L. Zhang, R. Linb, G. Yang, W.Wang, Y. Li, *J. Mol. Liquids.*, 2015, *203*, 98.

Thermodynamic and spectroscopic study of the interaction of Al $^{3+}$ with olygophosphate ligands in aqueous solution

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Interest in the chemistry of aluminium complexes has increased in recent years. Compounds of aluminium occur widely in nature. Aluminium salts and compounds are toxic to animals and humans. They are involved in various disorders of the human skeleton, nervous system and blood[1]. We have studied the interaction between Al^{3+} and ortho-phosphate (PO_4^{3-}), pyro-phosphate (*PP*), tri-polyphosphate (*TPP*) and hexa-metaphosphate (*PolyP*) in aqueous solution, as these systems are relevant to both biological systems and to the environment. Models have been developed by processing potentiometric titration data to determine the stability constants of the species which are present in equilibrium mixtures. Thermodynamic parameters were obtained from data obtained with calorimetric titrations. Data were obtained at 298.15 K with a background electrolyte (NaCl) concentration in the range 0.15 - 1 mol L^{-1}. The range over which useful data could be obtained for the Al^{3+}-PO_4^{3-} system was limited by precipitate formation, even in acidic conditions. With the oligophosphates measurements could be made up to pH 9. The species AlL was found to be formed with all ligands. Other species identified include Al(LH), $Al(LH_2)$, AlL_2 and AlL_2H. The complex AlL(OH), was also found with all oligophosphate ligands. Some derived numerical data are shown in the table. The parameter $pL_{0.5}$ is derived from stability constant values to provide an index of the total sequestering power of a ligand towards a metal ion[2].

Thermodynamic parameters (298.15 K, I = 0.15 mol L^{-1})

Ligand	PO_4^{3-}	$P_2O_7^{3-}$	$P_3O_{10}^{5-}$	$P_6O_{18}^{12-}$
$\log\beta_{AlL}$	14.07	13.53	14.11	8.42
ΔH^{θ}_{AlL} /kJ mol^{-1}	10.2	15	25	43
$pL_{0.5}$ at pH 5	5.73	9.44	11.27	7.36

As expected for hard-hard interactions between Al^{3+} and O-donor ligands, the contribution to the standard free energy change is dominated by the entropy contribution. The chemical model for the Al^{3+}-*TPP* system and some formation constant values were confirmed with data obtained from ^{31}P NMR measurements. Chemical shift values for the individual species AlL, AlL_2 and AlL(OH), were calculated by means of HypNMR[3]. It appears that *TPP* is acting as a bidentate ligand. For *PP*, *TPP* and *PolyP* ligands, the dependence of formation constants on ionic strength over the 0.1 $\leq I$ / mol $L^{-1} \leq 1$ range was calculated using a Debye-Hückel type equation.

References
1. K. Atkari, T. Kiss, R. Bertani, R. B. Martin, Interactions of Aluminum(III) with Phosphates, Inorg. Chem., 35, (1996), 7089.
2. A. Gianguzza, O. Giuffrè, D. Piazzese, S. Sammartano, Aqueous solution chemistry of alkyltin(IV) compounds for speciation studies in biological fluids and natural waters, *Coord. Chem. Rev*., (2012), 256, 222.
3. C. Frassineti, S. Ghelli, P. Gans, A. Sabatini, M. S. Moruzzi and A. Vacca, Nuclear Magnetic Resonance as a Tool for Determining Protonation Constants of Natural Polyprotic Bases in Solution, *Anal. Biochem*., (1995), 231, 374.

Study of the interaction between water-kefir grains and metals in solution

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Kefir grains are a consortium of symbiotic microorganisms, mainly consist of different lactic acid bacteria (LAB) and yeasts. The grains consist of a sugar polymer (dextran), that host the microbial consortium, and the single grains have a cauliflower like shape of 5–20 mm in diameter, a transparent appearance and an elastic structure[1]. The kefir grains ferment hexose sugars (such as sucrose) producing primarily lactic acid, ethanol and metabolites, that are released in the growth media. So, the final liquid drink, known as water-kefir too, contains many other interesting substances, among these acetic acid, glycerol, mannitol, vitamins, essential amino-acids and mineral elements. Because of nutraceutical benefits, studies concerning kefir are increasingly frequent in the last years. In addition, new researches have also showed how kefir grains are able to complex metallic cations present in the environment of fermentation but the mechanism is not fully understood. Therefore, the main goal of this study is deeper understanding of kefir complexing ability in order to assessment possible applications in health and environmental fields. To this end, the interaction between water-kefir grains and metallic ions was studied. Assuming that the proteins present on the superficial layer of the granules (S-layer proteins) are responsible of the complexing of the metallic cation, the research was initially focused into the nature of complexes, and studies of Raman spectroscopy and electronic paramagnetic resonance (EPR) were employed to investigate this aspect. Moreover, kinetic studies were carried out. The metals studied were mainly Pb, Ni, Cu, Mn, Cr(III) and Cr(VI). Pb, Ni and Cr are toxic elements, while Cu and Mn are paramagnetic elements present in natural water. In addition, other metallic species were investigated, such as Ca, K, Mg and Na. These elements are found in significant amount in the kefir grains and in water used for the water-kefir preparation. The study of the interaction between kefir grains and Cr(III) and Cr(VI) intends to understand if a different sequestering capacity towards Cr(III) and Cr(VI) exist, and if kefir grains present a reducing capacity towards Cr(VI). The studies of kinetic related to each metal were carried out putting the water-kefir colonies in sucrose and water solutions with different concentrations of single metal. The pH and metal concentrations were measured at different intervals of time and this last analysis was conducted by ICP-OES. The obtained data showed the different exchange rate of metals and the different variation of acidification rate. It can be seen that the presence, the metal type and its concentration cause metabolic interference, modifying the physiological trend of pH. This effect is more evident in the first hours after addition of the metal, afterwards to its absorption, especially at high concentrations of cations. However, the adsorption process is reversible, since the metal is partially released after long contact times (24 h) and pH reaches the physiologic value (approx. pH= 3).

References

1. Arslan, S. A review: chemical, microbiological and nutritional characteristics of kefir. CyTA - J. Food 13, 340–345 (2014).

Speciation of Al^{3+} in the presence of ligands of industrial, biological and environmental interest

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This contribution is the result of an investigation on the binding and sequestering ability of three ligands different in terms of chemical point of view and of fields of application. The ligands under study are:

- Gantrez®AN169 (H_4*GTZ*), a synthetic copolymer of methyl vinyl ether and maleic anhydride, having several applications in industrial, cosmetics, pharmaceutical and oral care product fields[1];
- citric acid (H_3*Cit*), a low molecular weight organic acid, with a well-known biological role[2];
- orthosilicic acid (H_4SiO_4), an inorganic compound and the main form of bioavailable silica for humans and animals[3].

Their interactions and binding ability towards Al^{3+} was investigated by performing potentiometric (ISE-H^+) measurements at different conditions of metal-ligand concentration ratio (c_M/c_L), temperature ($283.15 \leq T/\mathrm{K} \leq 318.15$) and ionic strength ($0.10 \leq I/\mathrm{mol\ L^{-1}} \leq 1.00$) in $NaCl_{(aq)}$, the main inorganic component of mostly natural and biological fluids. Different speciation models were determined taking into account the acid-base properties[4-7] of the ligands and of the metal cation. For all the systems the formation of a common species, namely the protonated Al*L*H, was observed. The investigation on the Al^{3+}/GTZ^{4-} and Al^{3+}/Cit^{3-} interactions showed also the formation of other species with different stoichiometry ($Al_pL_qH_r$), such as simple metal-ligand, polynuclear and mixed hydroxo species. The dependence of the stability constants on ionic strength and temperature was modelled by means of a Debye-Hückel type equation. From the formation enthalpy changes values, it was evidenced that all the reactions are endothermic in nature and the entropic contribution can be considered the driving force for the stability of the complexes.

Furthermore, the sequestering ability of the ligands towards Al^{3+} was investigated by the determination of an empirical parameter, the $pL_{0.5}$, already proposed by the research group[8]. It represents the total concentration of ligand necessary to sequester the 50% of a metal cation present in trace in solution and can be described by a sigmoid type Boltzmann equation. The analysis of the $pL_{0.5}$ values determined at different experimental conditions showed that in all the cases the sequestering ability increases increasing the pH and the temperature, whilst it decreases increasing the ionic strength in $NaCl_{(aq)}$.

References
1. Acevedo, R. A.; Machón, L.; Chávez, N., *J. Contemp. Dent. Pract.* 2009, 10, (*6*), E033-40.
2. Mailloux, R. J.; Bériault, R.; Lemire, J.; Singh, R.; Chénier, D. R.; Hamel, R. D.; Appanna, V. D., *PLoS ONE* 2007, 2, (*8*), e690.
3. Jurkic, L. M.; Cepanec, I.; Pavelic, S. K.; Pavelic, K., *Nutr. Metab.* 2013, 10, (*1*), 2.
4. Bretti, C.; Cigala, R. M.; Crea, F.; De Stefano, C.; Gattuso, G.; Irto, A.; Lando, G.; Milea, D.; Sammartano, S., *J. Chem. Eng. Data* 2017, DOI: 10.1021/acs.jced.7b00101.
5. Berto, S.; Crea, F.; Daniele, P. G.; De Stefano, C.; Prenesti, E.; Sammartano, S., *Radiochim. Acta* 2012, 100. 6. Martell, A. E.; Smith, R. M.; Motekaitis, R. J., National Institute of Standard and Technology: Garthersburg, MD, 2004.
7. Cigala, R. M.; De Stefano, C.; Giacalone, A.; Gianguzza, A., *Chem. Speciation Bioavailability* 2011, 23, 33-37.
8. Crea, F.; De Stefano, C.; Foti, C.; Milea, D.; Sammartano, S., *Curr. Med. Chem.* 2014, 21, 3819.

Interaction of 5-hydroxypyridinone derivatives with Fe(III), Ga(III), Al(III), Cu(II) and Zn(II) ions.

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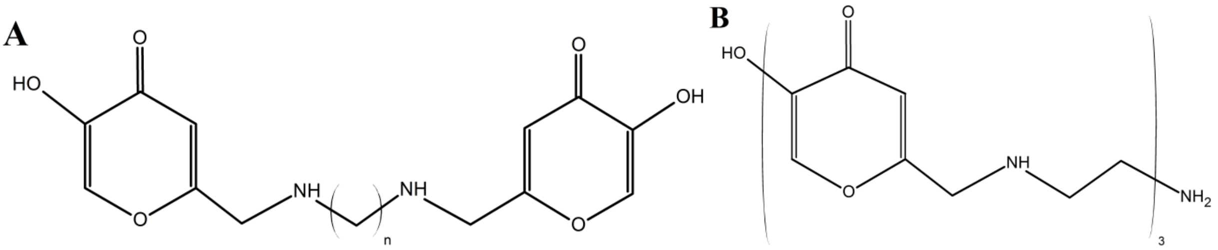
The hydroxypyrones and the close congeners, hydroxypyridinones, are a particularly versatile class of ligands for biomedical use[1]. Key features of these ligands are: a six-membered ring, with a ring N or O atom either *ortho* or *para* to a ketone group, and two *ortho* exocyclic oxygen atoms. Readily functionalizable, the hydroxypyrones allow one to achieve a range of di- and trivalent metallocomplex stabilities and can include tissue or molecular targeting features by design[2]. Hydroxypyrone applications vary from metal ion removal or supplementation, contrast agents in imaging applications, to mobilization of undesirable excess of metal ions [1-3]. Four new kojic acid derivatives (Scheme 1) were synthesized and their dissociation constants as well as theit ability toward Fe(III), Ga(III), Al(III), Cu(II) and Zn(II) ions was evaluated using potentiometric, calorimetric, NMR and UV–Vis techniques. Structural information on the complex formation equilibria have been obtained from 1D and 2D NMR study. The donor atoms involved in the coordination of Fe(III), Ga(III) and Al(III), Cu(II) and Zn(II) ions are (O, O) the same at acidic and neutral pH values, even if from the complexation competition study the ligand appears to be more selective toward Fe(III) ions supporting that it can be used as an iron chelating agent. The involvement of N-donor atoms at high pH in Cu(II) and Zn(II) coordination has been determined by using UV–Vis or NMR techniques.



Scheme 1. Molecular structures of (A) S1 (n=2), S2 (n=3), S3 (n=4) and (B) S4.

References
1.V. M. Nurchi, G. Crisponi, J. I. Lachowicz, S. Medici, M. Peana and M. A. Zoroddu, Journal of Trace Elements in Medicine and Biology, 2016, 38, 10-18.
2. K. H. Thompson, C. A. Barta and C. Orvig, Chemical Society Reviews, 2006, 35, 545-556.
3. G. Crisponi and M. Remelli, Coordination Chemistry Reviews, 2008, 252, 1225-1240.

Survey of the solubility data of organic molecules. Classification and modeling of the factor influencing Setschenow coefficients in several ionic media.

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In this contribution, a survey of the total and specific solubility of several organic molecules is performed. Even if the importance and the impact of the knowledge of the solubility is obvious (not only for the field of analytical chemistry), the experimental determination of these parameters, and of the Setschenow coefficient[1] is often limited to few articles per year, and consequently the number of indexed scientific journals interested on these topics is generally decreasing. As an example, no database are available for this kind of information. For this purpose, a quantitative analysis of the factors influencing the solubility and the modeling of the Setschenow coefficient can be helpful to rationalize the results published in the past, to give tools to estimate the solubility of new compounds, and predict the Setschenow coefficient, the parameter that accounts for the increase (salting-in) or decrease (salting-out) of the solubility when the concentration of the background salt increases. Literature data, relative to total and specific solubility on pure water, together with Setschenow coefficients in different ionic media, were collected and critically analyzed, assigning a weight on the basis of the reliability of the experimental determination. Then, each datum was assigned to a class, based on chemical properties, such as structure (linear or cyclic), functional group (carboxylates, amines or mixtures), number of carbon atoms, values of the protonation constants etc… Once the literature data are rationalized and classified, they can be modeled using empirical equations and principal component analysis to obtain quantitative information about the descriptors of the Setschenow coefficients and the solubility in pure water. The results will be tested to check the goodness of the fit and the models will be validated splitting the sample in a test set, containing 90% of the whole data, and an evaluation set, containing the remaining 10% of the sample.

The models obtained for the estimation of the Setschenow coefficients will be compared with the existing ones, such as those of Yu et al. (based on IEF-PCM calculations)[2], Xu et al. (based on QSPR studies)[3] and Ni and Yalkowsky (based on water/octanol partition coefficient)[4].

References

1. J.Z. Setschenow, Uber Die Konstitution Der Salzlosungenauf Grund Ihres Verhaltens Zu Kohlensaure, Z. Physik. Chem., 4 (1889) 117-125.
2. X. Yu, R. Yu, Setschenow Constant Prediction Based on the IEF-PCM Calculations, Ind. Eng. Chem. Res. 52 (2013) 11182−11188.
3. J. Xu, L. Wang, L. Wang, X. Shen, W. Xu, QSPR Study of Setschenow Constants of Organic Compounds Using MLR, ANN, and SVM Analyses, J. Comput. Chem. 32 (2011) 3241-3252.
4. N. Ni, S. H. Yalkowsky, Prediction of Setschenow constants, Int. J. Pharm. 254 (2003) 167–172.

Modulation of acid-base properties in fused-ring n-rich aromatics

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Heterocycles are key compounds of synthetic chemistry. This class of compounds shows many relevant applications in biochemical field[1], but recently they are playing a fundamental role as building blocks of active molecules in many fields of advanced materials: conducting polymers[2], organic field-effect transistors[2], Dye-sensitized Solar Cells (DSSC)[3], nonlinear optically active and liquid crystalline compounds[4], high energy compounds[5]. The [1,2,4]triazolo[3,2-c][1,2,4]triazole system is a fused-ring N-rich aromatic system with remarkable acid-base properties and tautomerism. It is possible to exercise a fine control of the tautomeric forms present in solution or in the solid state and of the acid-base properties in the fundamental and excited state, by acting on the electronic character of the group at position 7 of the heterobicycle. In fact the relative amount of the two singly protonated tautomeric forms (1*H*-3*H* and 2*H*-3*H*) can be finely tuned in such a way that only 1*H*-3*H* is present, or only 2*H*-3*H* or both. In the case of the phenol substituent (7-p-hydroxyphenyl), both tautomeric forms are present in comparable amount in solution; the two tautomers can also be selectively precipitated in different crystalline salts using suitable counterions[6,7]. In this work, we propose a study of acid-base properties of the structural isomers of the 4-methyl-7-(hydroxyphenyl)-2H-[1,2,4]triazolo[3,2,-c][1,2,4]triazole (Fig. 1). The hydrolytic equilibria have been studied at 25 °C in constant ionic medium NaCl 0.5 M/ethanol 4% (v/v) by recording UV-VIS spectra (absorption and emission) at different pH. The experiments have been performed as acid-base titrations at constant concentration of TT5, without varying the 0.5 M level of [Cl$^-$]. The pH investigated spans between 0.3 and 11. For each experimental point, the equilibrium free proton concentration was evaluated from the measured electromotive force at the ends of the galvanic cell *G.E. /T.S. /R.E.*, where *T.S.* indicates the Test Solution, *G.E.* is the glass electrode and *R.E.* is a reference electrode.

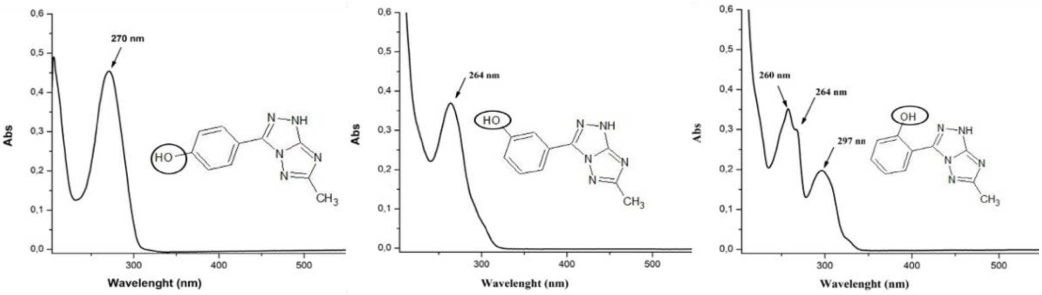

Figura 3 UV- VIS absorption spectra of three structural isomers register in NaCl 0.5M/ethanol 4% (v/v) at pH 4

References
1. V. Piccialli, S. D’Errico, N. Borbone, G. Oliviero, R. Centore, S. Zaccaria, Eur. J. Org. Chem. (2013) 1781-1789.
2. A. J. Heeger, Chem. Soc. Rev. (2010) 39, 2354-2371.
3. J. Li, A. C. Grimsdale, Chem. Soc. Rev. 39 (2010) 2399-2410.
4. S. Fusco, R. Centore, P. Riccio, A. Quatela, G. Stracci, G. Archetti, H.-G. Kuball, Polymer 49 (2008) 186-191.
5. Klapötke, T. M.; Schmid, P. C.; Schnell, S.; Stierstorfer, J. Chem. Eur. J. 2015, 21, 9219−9228.
6 R. Centore, C. Manfredi, S. Fusco, C. Maglione, A. Carella, A. Capobianco, A. Peluso, D. Colonna, A. Di Carlo J. Mol. Struct. (2015), 1093, 119-124.
7. C. Manfredi, A. Capobianco, S. Volino, M.V. Ferrara, A. Carella, S. Fusco, A. Peluso, J. Org. Chem. (2017) DOI: 10.1021/acs.joc.7b00380.

Oxidized G-C_3N_4 For the Photocatalytic H_2 Production From Glucose Aqueous Solution Under Solar Light

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In the past few years we have studied the application of various (waste) biomasses as the sacrificial agents to assist the photocatalytic H_2 production from water, using the well known Evonik P25 TiO_2, modified with Pt (1,2,3). In this work, we explored the photocatalytic behaviour of graphitic carbon nitride (g-C_3N_4), a novel organic semiconductor that is attracting great interest in view of the low cost preparation and its unique properties, such as visible light absorption (band gap 2.7 eV), high surface area 2D structure, chemical stability, and stronger reduction capability of photo-induced electrons compared to TiO_2 (4). The g-C_3N_4 catalyst was prepared by thermal condensation of dicyandiamide (500/650°C, 4 h, N_2 flow), then it was refluxed in 7.35 M HNO_3 solution under magnetic stirring (3 h) to obtain the oxidized material (o-g-C_3N_4). Both materials were characterized by X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and diffuse reflectance UV-Vis spectroscopy (DRS), and they were tested in aqueous solution in presence of glucose as biomass-representative sacrificial agent, using Pt as the co-catalyst by in situ photodeposition. Lab-scale experiments were carried out to investigate the variables potentially affecting H_2 evolution from various natural waters, that is catalyst amount, Pt loading, glucose concentration. Irradiation was performed on 28 mL capacity Pyrex glass containers, under simulated solar light (500 W/m^2, outdoor filter) and magnetic stirring (6 h). The evolved H_2 was quantified by headspace gas chromatographic analysis (TCD detector, Ar carrier gas). Considering the 2D structure of the catalyst, irradiation experiments were performed after sonication to enlarge the available surface area and to favor its suspension in the aqueous sample. Preliminary tests in distilled water indicated that o-g-C_3N_4 has a higher photocatalytic activity (about 20-fold) for H_2 production compared to g-C_3N_4, not further investigated. H_2 evolution from water was strongly enhanced by addition of glucose compared to pure water (0.2% from direct water splitting), while no H_2 was detected omitting the catalyst and/or the co-catalyst (as expectable). These results clearly show that o-g-C_3N_4 is effectively able to assist H_2 production from water under simulated solar light, in presence of a sacrificial biomass. The evolution profiles proved to be strictly dependant on the experimental conditions, with reaction yields favored by increasing glucose concentration and Pt loading, up to 0.1 M and 3 wt%, respectively. With regard catalyst concentration, H_2 production was strongly improved working with small amount of o-g-C_3N_4, that is 0.25 g/L. Under these conditions, H_2 yields up to 840 μmol/h per gram of catalyst were achieved, and further work will be undertaken testing environmental waters (river and sea waters), under natural sunlight (outdoor conditions). The results obtained from application of o-g-C_3N_4 are then critically compared to those observed using platinized commercial TiO_2, chosen as the reference catalyst. Additional characterizations will be performed (by BET surface area measures and X-ray photoelectron spectroscopy, XPS) in order to correlate the physical-chemical properties of the catalysts to the performance for H_2 photoproduction.

References
1. Int. J. Hydrogen Energy 39 (2014) 11433-11440.
2. Photochem. Photobiol. Sci. 13 (2014) 1410-1419.
3. Int. J. Hydrogen Energy 40 (2015) 4303-4310.
4. J. Mater. Chem. A 3 (2015) 23642-23652.

Photolytic and photocatalytic degradation of Glucocorticoids in water under simulated solar light

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Glucocorticoids (GCs) are anti-inflammatory drugs employed in human and veterinary medicines, sometimes as growth promoter. They are partially metabolized in hepatic and extrahepatic sites, and excreted by the kidney[1]. Their occurrence has been assessed in the aquatic compartment ranging from a few ng L^{-1} up to some tens of ng L^{-1} [2]. This indicates their ineffective removal by conventional wastewater treatment plants. Photodegradation is a significant tool for the abatement of persistent pollutants in water system. The photodegradation of some among the most frequently prescribed Glucocorticoids (Betamethasone, Cortisone, Dexamethasone, Hydrocortisone, Prednisolone, Prednisone, Triamcinolone acetonide) was investigated in tap water under simulated solar light, also in the presence of suspended TiO_2. The experiments were carried out in a lab-scale batch reactor at environment-significant concentration (50 µg L^{-1}) and at mg L^{-1} levels. Irradiated samples were analyzed by HPLC with electrospray ionization tandem mass spectrometry detector (HPLC-ESI-MS/MS) and by HPLC with UV detector, respectively. A first order kinetic was obeyed upon both direct photolysis and heterogeneous photocatalysis. The photoproduced intermediates profiles were followed by HPLC-ESI-MS/MS, after extraction with CH_2Cl_2 and evaporation of the eluate. For example, in Figure 1a and 1b the decomposition profiles of Dexamethasone under direct and TiO_2-promoted photolysis and the photoproducts profiles from direct photolysis are shown. Degradation rates were markedly faster by heterogeneous photocatalysis for all the drugs. This supports the contention that TiO_2 photocatalysis under simulated solar light is a convenient and efficient method for the remediation of pollutants. Photoproducts from both photolysis and photocatalysis will be identified to better clarify photodegradation path in the aquatic environment.

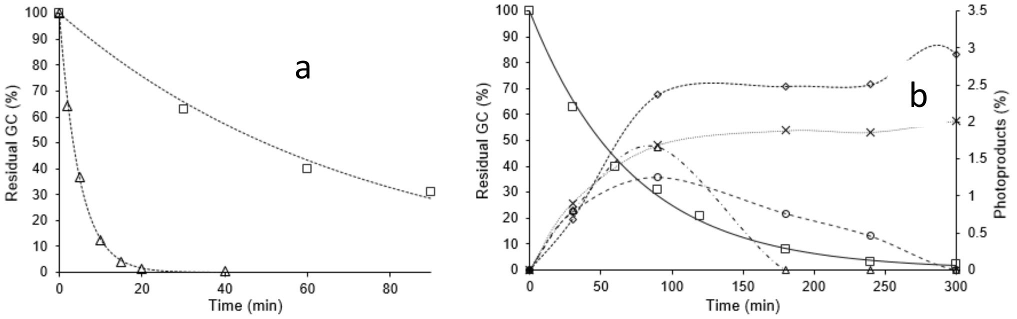

Fig.1. (a) Decomposition profiles of Dexamethasone (10 mg L^{-1}, tap water, simulated solar light) under direct (□) and TiO_2-promoted photolysis (△); (b) Dexamethasone (10 mg L^{-1}, tap water, simulated solar light) photoproducts profiles from direct photolysis.

References
1. Glucocorticoids, Goulding N.J., Flower R.J., ed. Birkhauser (2013).
2. Chemosphere 144 (2016) 1162-1169.

Determination of Volatile Organic Compounds in Exhaled Breath of Heart Failure Patients by Needle Trap Micro-Extraction Coupled to GC-MS/MS

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An innovative approach based on Needle Trap Micro-Extraction coupled to GC-MS/MS technique was developed and used to monitor Volatile Organic Compounds (VOCs) in exhaled breath of Heart Failure (HF) patients. HF is a complex clinical syndrome caused by a structural and/or functional cardiac abnormality. Patients hospitalized for HF are at high risk for re-hospitalization principally due to exacerbation of symptoms or signs of HF. Thus, a regular check of biomedical parameters is recommended for a suitable patient monitoring. With respect to the conventional clinical investigations (dosage of natriuretic peptides in serum, e.g. B-type or N-terminal pro-B-type natriuretic peptides, and transthoracic Doppler 2D echocardiography), breath analysis is an extraordinarily attractive approach for a most effective, easy, painless and non-invasive monitoring of patients suffering from HF. In the present work, the innovative and emerging technique based on Needle Trap Micro-Extraction was applied to determine VOCs in exhaled breath of HF patients. Needle Trap Devices (internal diameter 0.34 mm and length 6 cm) packed with 1 cm of Divinylbenzene, 1 cm of Carbopack X and 1 cm of Carboxen 1000 were used to collect and pre-concentrate VOCs in a single step. The Needle Trap Devices were then introduced in the injection system and VOCs were thermally desorbed and analysed by GC-MS/MS. The analytical figures of merit are discussed and the results obtained on 30 HF patients are presented.

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Tests on organic pollutants: DNA/BSA binding and micellar retention of two model PAHs and two model pesticides

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Organic pollutants as polycyclic aromatic hydrocarbons (PAH) and pesticides are nowadays ubiquitous[1]. PAH and pesticides are highly lipophilic and all at least suspected of carcinogenic effects[2,3]. Information on their toxic activity is often related to *in vivo* studies, whereas a detailed analysis of the mechanistic/chemical aspects of the binding to biosubstrates is sometimes missing. To contribute to this field and in the frame of our participation to PNRA (National Antarctic Research Program) we have carried out some tests on the binding of two PAH and two pesticides (Figure 1) to biosubstrates as natural DNA and the protein bovine serum albumin (BSA). The interaction with micelles and liposomes was also tested, both as to scale the lipophilicity of these species and to get information of the possible accumulation on membranes.

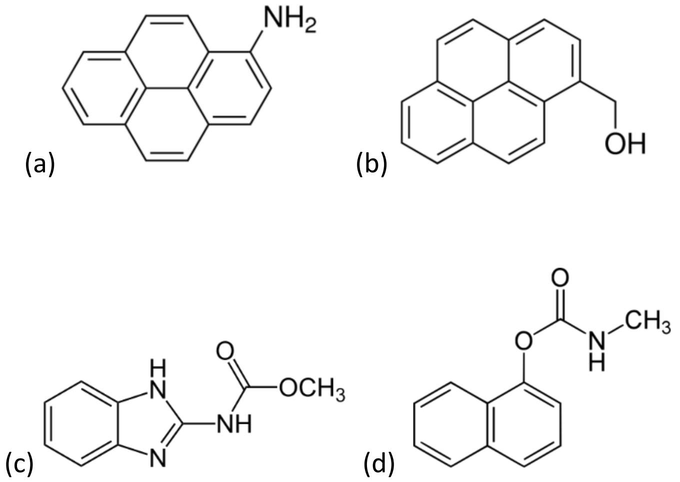

Figure 1. The PAH and pesticides tested: (a) 1-aminopyrene, (b)1-hydroxymetilpyrene, (c) carbendazim and (d) carbaryl.

The results collected show that the high hydrophobicity of these species turns into very high affinity for DNA. Absorbance and fluorescence titrations suggest complex binding modes that are discussed in relation with the different pollutant/DNA ratio. BSA binding is also found to occur in the case of the two PAH. Ultrafiltration coupled with absorbance spectroscopy enables the percentage of retention (R%) on the micelle/liposome be measured. R% dependence on the molecule and on the type of system (sodium dodecyl sulphate anionic micelles, TritonX-100 neutral micelles, dodecyl trimethyl ammonium chloride positive micelles and 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine liposomes) is discussed.

References
1. Lo Giudice A., Casella P., Bruni V., Michaud L.; *Ecotoxicology*, 2013, *22*, 240-250.
2.Yu H., *Journal of Enviromental Science and Health*, 2002, *20*, 149-183.
3. Alavanja M. C. R., Bonner M. R.; *Journal of Toxicology and Environmental Health Part B*, 2012, *15*, 238-263.

Analysis of Neurotoxin BMAA by Liquid Chromatography-High Resolution Mass Spectrometry: Over the Misidentification

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Since 1940's, the consumption of cycad seeds was associated with the increased incidence of amyotrophic lateral sclerosis (ALS) and Parkinson-like disease in the population of the Guam isles. The neurotoxin β-N-methylamino-L-alanine (BMAA), isolated from the cycad kernels, was hereafter suspected to be involved in these neurological diseases. Actually, this amino acid was produced by a cyanobacteria living in symbiosis with the cycad roots, and was then reported as a metabolite of various cyanobacterial species, so that its presence in algae and the consequent bioaccumulation in derived-food were considered to play a relevant role in such diseases. Anyway, the widespread reports of BMAA were impaired by analytical false-positives due to the isomeric amino acid α-,γ-diaminobutyric acid (DAB)[1]. Figure 1 shows the structures of the two compounds.

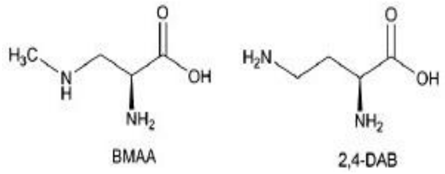

Figure 1: structures of BMAA and its isomer α-, γ-diaminobutyric acid (DAB)

As a matter of fact, the use of mass spectrometric (MS)-based methods did not eliminate the possibility of an overestimation of the neurotoxin concentration, since the simultaneous presence of two isomeric hydrophilic compounds hindered the use of the conventional reversed phase chromatographic separation.

A method based on liquid chromatography coupled to high resolution tandem mass spectrometry (LC-HRMS/MS) able to reliably quantify BMAA was developed. Specific fragment ions were highlighted for BMAA and DAB. After the evaluation of different chromatographic strategies, a satisfactory separation of BMAA from DAB was accomplished by using a mixed cationic-reverse phase column (Figure 2).

The method was validated in two different matrixes, i.e. water and plasma samples, in order to propose an analytical tool for monitoring occurrence of BMAA in environment and its possible distribution in biological samples. The analyses of BMAA in extremophile cyanobacteria typically produced in hot springs from Abano (Padova, Italy) and in the Antarctic region were also performed.

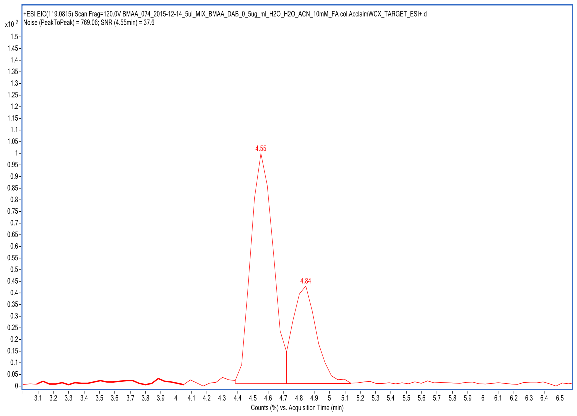

Figure 2: LC-MS chromatogram related to the final experimental condition for analyzing BMAA.

Reference
1. E. Faassenn, "Presence of neurotoxins BMAA in aquatic ecosystems: what do we really know?"; *Toxins*, 2014, *6* (3), 1109-1138.

Thallium Stimulates Ethanol Production in Immortalized Hippocampal Neurons/Cell Line

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Thallium (Tl), is a soft metal and the oxidation states are I and III. Thallium is more toxic to humans than mercury, cadmium, lead, copper, or zinc, and is responsible for many accidental, occupational, deliberate, and therapeutic poisonings since its discovery in 1861[1].

Mechanistically thallium is known to bind to sulfhydryl groups of proteins and mitochondrial membrane, thereby interfering with a range of enzyme reactions (the vital potassium-dependent processes, substitution of potassium in the (Na^+/K^+)-ATPase, pyruvate kinase, ATPase, aldehyde dehydrogenase)[2] and leading to a generalized poisoning including ligand formation with protein sulfhydryl groups and inhibition of cellular respiration[3,4]. Since Tl^+ and K^+ are both univalent ions with similar ionic radii, Tl is able to interfere with potassium-dependent processes, and then mimics potassium in its movement and intracellular accumulation in mammals[5]. Even if the neuronal Tl toxicity is well known[6,7], at the present, no few experimental data are available on Tl-induced alterations of neuronal metabolism evaluated with HS-GC-MS or HPLC analytical techniques. In this work, we present the results of such an analysis on immortalized hippocampal neurons (HN9.10e cell line). We chose to investigate Tl effects on this neuronal cell line since it shares a large number of structural and functional features with primary hippocampal neurons and, consequently, it is a reliable *in vitro* model of one of the most vulnerable regions of central nervous system, particularly susceptible to the toxic action of drugs or poisons and also severely damaged by neurodegenerative diseases. By HS-GCMS and HPLC analysis, we examined both the acute and the long-term effects of Tl exposure, finding remarkable and unexpected variations in metabolite composition of cell culture medium (CCM) variations in volatile organic compounds (VOCs) released in CCM. The increase of lactate and EtOH in Tl-exposed cell cultures suggests significant alterations in energy metabolism[8]. We would suggest in HN9.10e cells the activation of an ancestral mechanism to survive hypoxia/mitochondrial impairment, a kind of "functional hypoxia", in which the EtOH production is the key adaptation that allows a continued high level of glycolysis[9].

References

1. US Environmental Protection Agency; *Toxicological Review of Thallium and Compounds* (CAS No.7440-28-0), EPA/635/R-08/001F. http://www.epa.gov/iris: 2009.
2. Kayne F. J.; *Archives of Biochemistry and Biophysics*, 1971**,** *143* (1), 232-239.
3. Douglas K. T., Bunni M. A., Baindur S. R.; *International Journal of Biochemistry*, 1990, *22* (5), 429-438.
4. Caracelli I., Haiduc I., Zukerman-Schpector J., Tiekink E. R. T.; *Coordination Chemistry Reviews*, 2014, *281*, 50-63.
5. Viraraghavan T., Srinivasan A.; in *Encyclopedia of Environmental Health*, Elsevier: Burlington, 2011; pp 325-333.
6. Nava-Ruiz C., Mendez-Armenta M.; in *Pollutant Diseases, Remediation and Recycling*, Lichtfouse E., Schwarzbauer J., Robert D.; Eds. 2013; Vol. 4, pp 321-349.
7. Repetto G., Sanz P.; Repetto M.; *Toxicology in Vitro*, 1994, *8* (4), 609-611.
8. Gray E., Larkin J. R., Claridge T. D. W., Talbot K., Sibson, N. R.; Turner, M. R.; *Amyotrophic Lateral Sclerosis and Frontotemporal Degeneration*, 2015, *16* (7-8), 456-463.
9. Van Waarde A., Van den Thillart G., Verhagen M.; in *Surviving Hypoxia: Mechanisms of Control and Adaptation*, P. W. Hochachka, P. L. L., T. Sick, M. Rosenthal & G. Van den Thillart (Eds.), Ed. CRC Press: Boca Raton, 1993; pp 157-170.

Fluorescent Core-Shell Molecularly Imprinted Nanoparticles for Detection of Sphingosine 1-Phosphate

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Sphingosine 1-Phosphate (S1P) is a biologically active lipid that plays a crucial role in several cellular processes such as growth, proliferation, motility and apoptosis. It is known that high S1P concentrations in the circulation (blood and lymphatic fluid) is correlated with cancer growth[1]. This highlights the need for selective and sensitive means to detect this biomarker for the diagnosis of tumors. Presently, the most used detection methods are based on HPLC separation of fluorophore-modified S1P and LC-MS/MS, procedures that require time consuming steps and expensive instruments. In this context, the concept of fluorescent molecularly imprinted polymers (MIPs)[2] can be very useful to develop a selective, sensitive, fast and low-cost detection method for S1P. We here report a molecular imprinting strategy for the detection of S1P based on MIPs, prepared using fluorescent monomers capable of reporting binding events real time. The MIP was characterized by FT-IR, SEM and DLS. Preliminary fluorescence tests show greater selectivity of MIP for S1P in comparison to the template and other molecules containing phosphate group. Further investigation of the recognition behaviour will be carried out in different solvents, with different ratios, in order to evaluate a possible application with real samples, such as human serum. For the same purpose, X-ray Photoelectron Spectroscopy (XPS) analysis will be performed to obtain useful information about the interactions driving lipid recognition in these polymers.

References
1. N.J. Pyne, S. Pyne; *Nature Reviews Cancer;* 2010*;10*, 489-503.
2. Wei Wan, Mustafa Biyikal, Ricarda Wagner, Bçrje Sellergren, Knut Rurack; *Angew. Chem. Int. Ed.;* 2013, *52*, 1–6.

Extraction of UV Filters from Water Samples by Dispersive Solid Phase Extraction Using a New Magnetic Graphitized Carbon Material

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Magnetic solid phase extraction (mSPE) is one of the most promising new extraction methods for liquid samples before ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) analysis[1]. In mSPE, a composite material is constituted by a magnetic core covered by an organic or inorganic coating. In addition, some carbonaceous materials, such as activated carbon[2,3], carbon nanofibers[4], and multi-walled carbon nanotubes[5] were also modified by deposition of Fe_3O_4 onto the carbon material structure itself. Graphitized carbon blacks (GCBs) are a group of carbonaceous materials made from carbon blacks by heating them in an inert atmosphere, at T>2500 °C, which differ from one another by the surface area. GCB is considered to have homogeneous non-porous graphitic surface essentially oxygen-free giving, therefore, only van der Walls and π-π interactions. However, it has been demonstrated that a relatively small-portion of the surface is still contaminated by oxygen bound to graphitic crystallite edges[6]. In the present research, for the first time, the preparation, characterization and sorption capability of Fe_3O_4-GCB composite (mGCB) toward some compounds of environmental interest were investigated. First, GCB was oxidized with nitric acid, this resulting in a mild oxidation of some oxygenated heterogeneities already present on GCB surface. Then, the material was magnetized by a simple solvothermal synthesis of Fe_3O_4 on its surface. The magnetic composite showed a surface area of 55 $m^2\ g^{-1}$ and 55% of Fe_3O_4. The prepared mGCB was firstly tested as an adsorbent for the extraction from surface water of fifty pollutants, including estrogens, perfluoroalkyl compounds, UV filters and quinolones. The material showed good affinity to many of the tested compounds, except carboxylates and glucoronates; however, some compounds were difficult to desorb. Ten UV filters belonging to the chemical classes of benzophenones (seven) and p-aminobenzoates (three) were selected, and a method for determining these compounds in surface water by mGCB extraction followed by UHPLC-MS/MS analysis was validated and applied to eight surface water samples. The method was validated in terms of linearity, trueness, intra-laboratory precision and detection and quantification limits. In summary, the method performance (trueness, expressed as analytical recovery, 85-114%; RSD 5-15%) appears suitable for the determination of the selected compounds at level of 10-100 ng L^{-1}, with detection limits in the range of 1-5 ng L^{-1}. Finally, the new method was compared with a published one, based on conventional SPE with GCB, showing similar performance in real sample analysis. To the best of our knowledge, mGCB stable in aqueous medium has never been prepared, characterized and used to extract pollutants from environmental waters.

References
1. Wierucka M, Biziuk M.; *TRAC-Trend Anal. Chem.*, 2014, *59*, 50–58.
2. Liu L, Hao Y, Ren Y, Wang C, Wu Q, Wang Z.; *J. Sep. Sci.*, 2015, *38*, 1411-1418.
3. Diao C, Yang X, Sun A, Liu R.; *Anal. Methods*, 2015, *7*, 10170-10176.
4. Sarafraz-Yazdi A., Rokhian T, Amiri A, Ghaemi F.; *New J. Chem.*, 2015, *39*, 5621-5627.
5. Amoli-Diva M, Pourghazi K, Hajjaran S.; *Mater. Sci. Eng.*, 2016, *60*, 30-36.
6. Campanella L, Di Corcia A, Samperi R, Gambacorta A.; *Materials Chem.*, 1982, *7*, 429-438.

Ultrasound-Assisted Emulsification Microextraction for Analytical Determination

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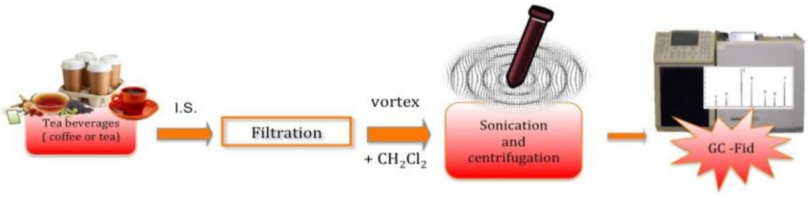
Ultrasound spectroscopy is a suitable tool for preparation and determination of food emulsion during processing. For such systems, a key parameter is the dispersed phase volume fraction. The dispersed volume fraction determines the relative proportion of oil and water in a product and of course has a pivotal role in the prediction of volumes during a microextraction process for analytical determination. An Ultrasound-Vortex-Assisted Dispersive Liquid-Liquid Micro-extraction procedure coupled with Gas Chromatography-Flame Ionization Detector is proposed for a reliable and sensitive analysis of phthalate esters in tea beverages[1]. Phthalates esters can be found in a wide range of products, including adhesives and glues, tubing, and food packaging. These compounds are easily released into the environment, as they are not covalently bound to the mixtures where they are used, in particular in hot drinks. Phthalate esters were extracted from samples (fresh prepared infusions of coffee and tea), using small amounts of CH_2Cl_2 (extraction solvent)[2]. The solution was vortexed, then kept in an ultrasound bath (40 kHz of ultrasound frequency and 110 W for 10 min at room temperature), finally the sample was centrifuged at 5000 rpm for several minutes. The bottom phase of the chlorinated solvent was separated from the liquid matrix and the determination of PAEs was performed by a GC Fid. An Enrichment Factor of about 150-200 times with a good recovery was found. The efficiency of the liquid-phase micro-extraction process was affected by the samples peculiarity, therefore the analytical characteristics of the method were evaluated in the linear range 0.5-50 ng mL^{-1} [3]. The validation of the proposed method was according to the Commission Decision EC/657/2002 concerning the performance criteria of analytical methods.



References
1. Cinelli, G., Avino, P., Notardonato, I., Centola, A., Russo, M.V. Rapid analysis of six phthalate esters in wine by ultrasound-vortex-assisted dispersive liquid-liquid micro-extraction coupled with gas chromatography-flame ionization detector or gas chromatography-ion trap mass spectrometry (2013) Analytica Chimica Acta, 769, pp. 72-78.
2. Russo, M.V., Notardonato, I., Cinelli, G., Avino, P. Evaluation of an analytical method for determining phthalate esters in wine samples by solid-phase extraction and gas chromatography coupled with ion-trap mass spectrometer detector (2012) Analytical and Bioanalytical Chemistry, 402 (3), pp. 1373-1381.
3. Cinelli, G., Avino, P., Notardonato, I., Russo, M.V. Ultrasound-vortex-assisted dispersive liquid-liquid microextraction coupled with gas chromatography with a nitrogen-phosphorus detector for simultaneous and rapid determination of organophosphorus pesticides and triazines in wine (2014) Analytical Methods, 6 (3), pp. 782-790.

Centrifugal and Asymmetrical Field-Flow Fractionation for the analysis of ZnO particles in cosmetic products

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Zinc oxide (ZnO) is a versatile material used in many productive sectors, of which the rubber application accounted for the largest market share, followed by ceramics, chemicals, pharmaceuticals, cosmetics, personal care and agricultural products. In the cosmetic sector, ZnO is used as a colorant or bulking agent, but mainly as UV-blocker, soothing and protective coating against skin irritation and abrasion, analogously to its use in the pharmaceutical products, mostly as ointments and creams, where it carries out antibacterial, antimicrobial, disinfecting and drying actions.

The recent increase of nano-materials to enhance the quality of many products has determined the revision of many existing international regulations, either in the cosmetic and food sectors. The European Union (EU) Commission's Working Group on Cosmetics, in 2016, for example, stated that ZnO-NPs cannot be used in spray products, or if it used in dermal application, ZnO-NPs must have a median diameter of the particle number size distribution D50 (50 % of the number below this diameter) > 30 nm and D1 (1 % below this size) > 20 nm[1].

The size analysis of ZnO particles dispersed in cosmetic or pharmaceutical formulations is consequently now an important task that analytical methods should face[2], since they could be used to discriminate the presence of particles in the nano or/and micro form. This implies that the analytical methods should be able possibly to determine the particle size distribution or at least to contribute, for example through a separation, to its determination.There are a number of analytical methods that might be used to size the particles[3,4]. In many cases, the determination of the average particle sizes and the size distribution of particles incorporated in cosmetic products, requires a preliminary extraction step. This work has consequently two main aims, to study whether and how the extraction procedures should differ depending on the cosmetic matrices and to compare the separation performances of two FFF techniques, Centrifugal FFF (CF3) and Asymmetrical Flow FFF (AF4), both used for the particle size characterization. The separation performances of CF3 and AF4 are evaluated by analysing (i) two different types of pristine ZnO powdered particles, bare and superficially modified with triethoxycaprylyl silane, available on the market to formulate cosmetic products, (ii) four cosmetic creams formulated in-house, and (iii) three cosmetic commercial products, sold in Italy and Germany for the baby skin care.

References
1. COMMISSION REGULATION (EU) 2016/621 of 21 April 2016 - Official Journal of the European Union, L 106 Volume 59 22 April 2016, ISSN 1977-0677.
2. T. Linsinger, G. Roebben, D. Gilliland, L. Calzolai, F. Rossi, N. Gibson, C. Klein, Requirements on measurements for the implementation of the European Commission definition of the term "nanomaterial", JRC, 2012.
3. C. Contado "Nanomaterials in consumer products: a challenging analytical problem" Front. Chem. (2015) https://doi.org/10.3389/fchem.2015.00048.
4. C. Contado, Field Flow Fractionation techniques to explore the "nano-world" Anal Bioanal Chem. 409(10) (2017) 2501-2518.

Planar and Column High Performance Liquid Chromatography of Biologically Active Compounds Extracted from Leaves and Fruits of Cyclanthera pedata (L.) Schrab

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This communication reports the results of a recent study carried out to develop straightforward methods for the identification and quantification of phenolic compounds occurring in the leaves and fruits of *Cyclanthera pedata* Scrabs (Caigua), as well as in food supplements produced from this plant. Caigua is an ancient Peruvian plant belonging to the Cucurbitaceae family, which is grown for its edible mature fruit in many parts of Central America, South America and the Andes. It is found in the Caribbean Islands, Colombia, Bolivia, Peru and Mexico. Caigua is also an ancient medicinal plant whose use dates back to the Inca population. Nowadays, this plant is gaining market importance around the world due to its anti-inflammatory, hypoglycaemic and hypocholesterolemic properties. Recent scientific studies attribute the anti-hyperglycemic properties of Caigua to the high content of phenolic compounds, the most abundant class of secondary metabolites, and, in particular, to the glycosilated flavonoids subclass. The occurrence of phenolic compounds in the leaves and fruits of Caigua grown in Italy and Slovenia was investigated using both high performance liquid chromatography (HPLC) and high performance thin layer chromatography (HPTLC). Sample detection was performed by either photodiode array (PDA) spectroscopy or mass spectrometry (MS) with electrospray (ESI) ionization, used for obtaining structural information on the separated compounds and for their quantitative analysis. A special surface sampling probe was used for extracting the analyte on-line from the HPTLC plate to the ESI-MS instrument. The separations by HPTLC were carried out in normal phase mode using silica plates and mobile phases consisting of a variety of organic solvents in mixtures at different volume rates. HPLC was performed in reversed phase mode employing a narrow-bore C-18 column and a semimicro photodiode array detector (PDA) cell of 2.5 μL, in conjunction with a single quadrupole mass spectrometer, equipped with an electrospray ionization source (ESI-MS). The C-18 narrow bore column was eluted by a multi-segment gradient of increasing concentration of acetonitrile in water-formic acid solution that has been optimized on the basis of the results of a study carried out to evaluate the influence of mobile phase composition and gradient shape on separation performance and detection sensitivity by ESI-MS. The identification of individual phenolic compounds was performed on the basis of their HPTLC retention factor **(**R_f) and HPLC retention time and both UV-visible and mass spectra, acquired by PDA and ESI-MS, respectively. Different organic solvents and hydro-organic mixtures were tested for their efficiency to extract the phenolic compounds from leaves and fruits of *Cyclanthera pedata* grown either in Italy (Rome) or Slovenia (Ljubljana), as well as from commercially available food supplements. A HPTLC-DPPH method was developed in order to assess the antioxidant properties of the compounds occurring in the Caigua extracts and in food supplements produced from this plant. Pros and cons, as well as complementary aspects, of HPTLC and HPLC methods for the identification and quantification of biologically active compounds in plant extracts are illustrated and discussed.

Evaluation of excess and adsorption isotherms in chiral stationary phases

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The adsorption equilibria of trans-stilbene oxide (TSO) enantiomers have been studied on Whelk-O1 chiral stationary phases (CSPs) prepared on both core-shell and fully porous particles (FPPs)[1]. Three columns were used in this study: a 100x4.6 mm column packed with 1.8 µm FPPs, a 150x4.6 packed with 2.5 µm FPPs and, finally, a 150x4.6 packed with 2.6 µm superficially porous particles (SPPs).
Firstly, the preferential adsorption of the binary eluent components on the stationary phase (or, more precisely, their excess adsorption isotherms) was evaluated through the so-called minor disturbance method. This method is based on the perturbation of the adsorption equilibria of mobile phase components (in this case hexane and ethanol) through small injections of an excess of one of the two components, when a steady-state equilibrium between mobile and stationary phase is reached. The excess isotherm is then obtained by studying the relationship between the retention times of the so-called disturbance peaks and the composition of the mobile phase[2]. Afterwards, the adsorption isotherms of TSO enantiomers have been studied by modeling overloaded peaks measured under different experimental conditions with mobile phases made of pure hexane and 90/10 hexane/ethanol % (v/v). The isotherm parameters were obtained by iteratively solving the chromatographic mass balance equation adjusting the adsorption parameters until optimal matching between calculated and experimental profiles is reached[3].
Different isotherm models have been used to determine the best adsorption isotherm for TSO on the three columns studied. At 90/10 hexane/ethanol % (v/v) the best adsorption model was found to be the bi-Langmuir one (accounting for two different adsorption sites on the adsorption surface) for all the columns. On the contrary, at 100% hexane the heterogeneous Toth model (predicting a continuous adsorption energy probability density function) best describes the adsorption.

References
1. O. H. Ismail, L. Pasti, A. Ciogli, C. Villani, J. Kocergin, S. Anderson, F. Gasparrini, A. Cavazzini and M. Catani, J. Chromatogr. A, 1466 (2016), 96-104.
2. Y. Kazakevich, H.M. McNair, J. Chromatogr. Sci. 33 (1995) 321.
3. N. Marchetti, A. Cavazzini, L. Pasti, F. Dondi, J. Sep. Sci. 2009, 32, 727 – 7411.

UHPLC- HRMS Study of Glucosinolates in Cauliflower Waste Products

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Brassicaceae are considered a functional food due to them high content of bioactive compounds, mainly glucosinolates. Several studies have stressed the capacity of Brassica species to prevent some type of cancers, activity connected to the high concentration of glucosinolates in those vegetables. In fact, Glucosinolates are hydrolyzed by endogenous thioglucosidases, called myrosinases, to produce a wide range of degradation products (isothiocyanates, nitriles, epithiocyanates, oxazolidine- 2-thiones, and thiocyanates) with diverse biological activities[1,2].

Frequent consumption of high-GLS-content vegetables is associated with a lowered risk of cancer and cardiovascular disease.

During the processing of these vegetables, an amount of byproducts is produced. Regarding the byproduct proportion, leaves constitute about 50% of the total; the rest is mainly stem. These residues are responsible for important environmental problems in the industries[3] and diminishing their environmental impact has been the subject of an increasing concern in recent years.

However, just a few studies have been done on the waist products of cauliflower's. Nevertheless, the waste still represents a good source of nutraceuticals that can further be subjected to isolation processes.

The aim of this study is to asses different kind of glucosinolates extraction methods, comparing the 80°C extraction against the RT one. Subsequently the purpose is to set up the best chromatographic/mass spectrometric condition in order to characterize the whole glucosinolates composition of cauliflower by-products.

References
1 Kliebenstein D.J., Kroymann J., Brown P., Figuth A., Pedersen D., Gershenzon J., Mitchell-Olds T.; *Plant Physiol.*, 2001, *126*, 811.
2. Halkier B.A., Gershenzon J.; *Annu. Rev. Plant Biol.*, 2006, *57*, 303.
3. Bonilla F., Mayen M., Merida J.; *Medina, M. Food Chem.*,1999, *66*, 209.

Air assisted dispersive liquid-liquid microextraction with solidification of the floating organic droplets (AA-DLLME-SFO) and UHPLC-PDA determination of five antibiotics in human plasma of hospital acquired pneumonia patients

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The growing drug resistance of *Gram-positive* (e.g. *Staphylococcus Aureus*) and *Gram-negative* (e.g. *P. Aeruginosa*) bacteria has become, during the last decade, an issue of concern for clinicians. So far, the therapeutic drug monitoring (TDM) of antimicrobial agents could be a useful tool against drug-drug interactions and might increase the therapeutical efficacy in patients suffering from nosocomial infection. Assadi *et al.* in 2006 developed a novel microextraction techinque called dispersive liquid-liquid microextraction[1]. In this technique, a cloudy solution of fine organic droplets is formed when a mixture of extraction solvent (immiscible with water) and a dispenser solvent (miscible with both water and the extratant solvent) is rapidly injected into an aqueous solution sample containing the analytes. In DLLME, large surface contact between fine droplets and the analytes, speeds up the processes regarding mass-transfer of analytes from aqueous phase to organic phase which greatly enhances extraction efficiency[2]. Nevertheless, the extraction solvent used in DLLME is generally highly toxic (chlorobenzene, chloroform or carbon disulfide), not environmentally friendly and incompatible with reverse phase HPLC. Recently, in order to solve this problem, a new microextraction technique has been developed by using extracting solvents which have lighter density than water integrated with the solidification of the organic floating droplet (DLLME-SFO). DLLME-SFO is widely applied for environmental water samples but rarely it is used for the analysis of drugs in complex matrixes such as biological fluids. In the present work a fast, sensitive, precise and accurate method for the determination of MER, MET, CIP, LIN and PIP in human plasma by UHPLC-PDA using a combination of protein precipitation (PP) and air assisted dispersive liquid-liquid microextraction with solidification of the floating organic droplet (AA-DLLME-SFO) has been developed. Various extraction parameters including selection of extractant, amount of extractant, ionic strength, pH and extraction cycles, were tested and optimized. Chromatography was carried out using a Poroshell 120 SB C_{18} (50 x 2.1 mm I.D. 2.6 µm particle size) column and a gradient mobile phase consisting of ammonium acetate buffer (10 mM, pH 4.0) (eluent A); and a mixture of acetonitrile-methanol in a ratio (80/20) (eluent B). Ulifloxacin was used as internal standard. The method demonstrated good linearity with correlation coefficients, $r^2>0.9995$ for the drugs, as well as high precision (RSD%≤ 9.87%), accuracy ranged from -8.14% to +8.98. During the validation, the concentrations of the analytes were found to be stable after 3 freeze-thaw cycles and for at least 24 h after extraction. Subsequently, this method was used to quantify the drugs in patients with HAP in order to establish if the dosage regimen given was sufficient to eradicate the infection at the target site.

References
1. M. Rezaee, Y. Assadi, M.R.M. Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, Determination of organic compounds in water using dispersive liquid-liquid microextraction, J. Chromatogr.A 1116 (2006) 1-9.
2. M. Rezaee, Y. Yamini, A. Khanchi, M. Faraji, A. Saleh, A simple and rapid new dispersive liquid-liquid microextraction based on solidification of floating organic drop combined with inductively coupled plasma-optical emission spectrometry for preconcentration and determination of aluminum in water samples, J. Hazard.Mater 178 (2010) 766-770.

Quality by Design framework in the development of a capillary electrophoresis method for the enantioseparation and impurity determination of cinacalcet hydrochloride

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Cinacalcet hydrochloride (CIN) is the first agent of a new class of calcimimetic compounds, which act by decreasing the secretion of the parathyroid hormone by activating calcium receptors. CIN is the only approved drug by the US FDA in 2004 acting as regulator of ionized calcium and is marketed as single *R*-enantiomer, which is about 75 times more potent than its corresponding *S*-enantiomer. CIN is useful in the treatment of chronic kidney disease where hyperparathyroidism is a common complication of chronic pathologies[1].

In this study, a capillary electrophoresis (CE) method for the simultaneous determination of the enantiomeric purity and of impurities of CIN has been developed following the Quality by Design principles[2]. Comparing to HPLC, CE utilizes the wide spectrum of chiral selectors as buffer additives for chiral separation without the need for expensive columns. Moreover, CE mostly provides shorter analysis time and better resolution and offers the advantage of altering the enantiomer migration order based on the change of the type of chiral selector. The most commonly used chiral selectors are the cyclodextrins (CDs), due to their wide variety of cavity size, side chain, degree of substitution and charge.

In the scouting phase of the development, preliminary experiments were carried out to select the separation operative mode and to identify a suitable chiral selector in order to reach an adequate selectivity. Among the tested CDs, (2-carboxyethyl)-β-CD and (2-hydroxypropyl)-γ-CD (HPγCD) showed chiral resolving capabilities at lower concentration values.

The best results were obtained by using solvent modified capillary zone electrophoresis with the addition of HPγCD. Voltage, buffer pH, concentration of methanol as organic modifier and concentration of HPγCD were investigated as critical process parameters. Critical quality attributes were represented by the critical resolution value between the enantiomers and analysis time. A Box-Behnken Design for four factors allowed the contour plots to be drawn and the design space to be identified with a desired probability level $\pi \geq 90\%$.

The working conditions, with the limits of the design space, corresponded to the following: capillary length, 48.5 cm; temperature, 18 °C; voltage, 25 kV (23-28 kV); background electrolyte, 150 mM phosphate buffer pH 2.8 (2.7-3.0), 3.1 mM (2.2-4.0 mM) HPγCD; 2% (0.0-7.0 v/v%) methanol. Applying the selected conditions, the full separation of analytes was obtained in about 10 min. The method was validated and finally applied to a real sample of CIN tablets.

References
1. W.D. Fraser, Hyperparathyroidism. Lancet 2009, 374:145-158.
2. S. Orlandini, S. Pinzauti, S. Furlanetto. Application of quality by design to the development of analytical separation methods. Anal. Bioanal. Chem. 2013, 405:443-450.

Quality by Design approach in the development of an UHPLC method for the analysis of selected polyphenols in *Diospyros Kaki*

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The development of an UHPLC method for the analysis of selected polyphenols in Diospyros kaki, using a triple quadrupole mass spectrometer as detector, is presented. The optimization of the method was performed through the principles of Quality by Design, consisting in the implementation of tools like risk assessment and multivariate strategies.

During the method scouting phase, different types of chromatographic columns were tested, and on the basis of the obtained selectivity an Acquity BEH UHPLC C18 was selected. The Critical Quality Attributes (CQA) were the critical resolutions of some isobaric compounds and analysis time. The Critical Process Parameters (CPP) were selected using the Ishikawa's diagram and were related to the characteristics of both the mobile phase and the column: flow, temperature, initial mobile phase composition, formic acid percentage in eluents, type of organic eluent and gradient. The effects of the CPPs on the CQAs were evaluated by a multivariate strategy, at first using a screening phase and then Response Surface Methodology (RSM). In the screening phase the knowledge space was investigated by an asymmetric screening matrix. Graphic analysis of the effects made it possible to set the type of organic solvent (methanol) and the optimal value for the flow, and in addition to select new experimental domains for the other involved CPPs. In the RSM the postulated quadratic models were calculated by means of Doehlert Design and were graphically represented by contour plots. The search for the global optimum zone was performed by the sweet spot plots, which were analysed in order to identify the zones where the multidimensional combinations of the CPP values allowed the desired values for all the CQAs to be obtained (resolution values ≥ 1, analysis time ≤ 20 min). Hence, the Design Space was identified as the multidimensional combination of the CPPs that satisfied the requirements for the CQAs, with a probability $\pi \geq 90\%$.

The method was validated and applied to real samples obtained by the extraction of Diospyros kaki flesh from two different cultivars (*Rojo Brillante* and *Kaki Tipo*) and processed in different ways (fresh fruit without any treatment, treated with ethylene, treated with CO_2). The results showed the remarkable concentration of some compounds (i.e. gallic acid, (+)-catechin, caffeic acid, *p*-coumaric acid, phloridzin), in agreement with literature data. Furthermore, compounds that have not been previously reported were found, including salycilic acid, luteolin, phloretin as well as ellagic acid, that was quantified in high concentration and the presence of which in persimmon was only reported occasionally in the peel of this fruit.

A rapid detection method of 2-dodecylcyclobutanone in irradiated exotic fruit by gas-chromatography / mass-spectrometry (GC-MS) coupled with solid phase microextraction (SPME) technique

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Exotic fruit production represents more than 40% of world fruit production in the world. Exporting exotic fruit worldwide has been made a reality by treating it with ionizing radiation, at the commercial dose levels in the range from 0.5 to 1.5 kGy. The food processing is mainly aimed at reducing spoilage, enhancing hygienic quality and at extending shelf life of treated products with negligible effects on the nutritional profile[1]. According to European legislation[2] any irradiated food, or food containing an irradiated ingredient within the EU must carry the word "irradiated" in a prominent position either as part of the main label or next to the ingredient that has been irradiated. It may also (optionally) show the international icon for irradiated food called the "Radura" symbol. There are several standardized techniques for the detection of the radiation treatment on food based on physical, chemical and biological changes. Among confirmatory methods the European standard EN 1785:2003[3] is able to detect irradiated fatty foods and it is based on the determination of 2-alkylcyclobutanones (2-ACBs), a unique radiolytic compounds formed after the irradiation of lipids components. This method, validated for a limited number of matrices, namely raw chicken, pork, liquid whole egg, salmon and Camembert, is based on the Soxlhlet extraction with hexane of the food lipid fraction, followed by the purification of the lipid phase on a deactivated Florisil column and the detection of 2-ACBs by GC-MS. The major limitations of the EN 1785 method are the Soxhlet extraction step, requiring the use of a large amount of solvent and a long extraction time (about 6 h), and the Florisil column clean-up stage showing a poor capacity to retain fat[4]. In this work, it was set up and validated an alternative method to identify the 2-dodecylcyclobutanones (2-DCB), resulting from the radiolysis of the palmitic acid, extracted by head-space solid-phase micro-extraction (HS-SPME) and detected by GC-MS. Although the HS-SPME-GC/MS technique has been applied on food of animal origin[5] a no study on plant origin food has been reported. Therefore a practical method to detect irradiated exotic fruit, analyzing mango and papaya seeds and avocado pulp, was proposed. Above specific components of food (seeds or pulp) were selected on the basis of their palmitic acid content. Both 2-DCB extraction procedure with a PDMS fiber and quantification of DCB relied on a matrix-matched calibration curve, using an internal standard (IS), was performed. The quantification of DCB and IS by GC/MS analysis was carried out in the SIM mode checking the presence of quantifier ions 98 m/z and 112 m/z in the ratio of 4-4.5:1. Finally main validation parameters such as specificity, LOD, LOQ, precision, intermediate precision and signal stability over a commercial shelf life, were determined. In conclusion an alternative method to current standard EN 1785[3] was successfully developed and applied to detect irradiate exotic fruit. Furthermore the proposed sensitive, rapid and solvent free technique could be extensively used for routine analysis in official controls required by European Commission.

References:
1. Shahbaz H. M. et al. (2016). "Worldwide Status of Fresh Fruits Irradiation and Concerns about Quality, Safety, and Consumer Acceptance" CRC CR REV FOOD SCI, Volume 56 (11).
2. DIRECTIVE 1999/2/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 22 February 1999 on the approximation of the laws of the Member States concerning foods and food ingredients treated with ionizing radiation
3. EN 1785:2003. (2003). Foodstuff Detection of irradiated food containing fat. Gas chromatographic/mass spectrometric analysis of 2-alkylcyclobutanones. European Committee for Standardization.
4. Crews C. et al. (2012). Analysis of 2-alcylcyclobutanones for detection of food irradiation: Current status, needs and prospects. Journal of Food Composition and Analysis. 26, 1-11.
5. Soncin et al. (2012). Improved determination of 2-dodecylcyclobutanone in irradiated ground beef patties by gas-chromatography–mass-spectrometry (GC/MS) coupled with solid-phase microextraction (SPME) technique. Food Chemistry 134 (2012) 440–444.

Protein analysis by two-dimensional LC using size-exclusion and reverse phase chromatography with column switching

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Over the years, two-dimensional Liquid Chromatography (2D-LC) has played a key role in the field of proteomics for the analysis and isolation of proteins from complex matrices, before their characterization by Mass Spectrometry[1,2]. In 2D-LC method development, a large number of experimental variables have to be extensively studied to take full advantage of the claimed features of the chromatographic separations[3]. In the last decade, significant improvements in LC column technology and instrumentation have been made and the introduction of superficially porous particles opened new possibilities in terms of speed and resolution.
Here an automated method combining size exclusion with reverse phase chromatography and UV detection is proposed for protein separations in food samples. For the first dimension separation, a size-exclusion column, packed with 3 μm ultra-pure silica particles densely bonded with a proprietary hydrophilic surface chemistry, was used, ensuring high efficiency and resolution. A reversed phase widepore column was used for the second dimension separation, based on core-shell particle technology that provides striking increases in peak capacity and resolution at lower backpressures. Different collection trap systems were placed on a 10-port switching valve and tested to focus the proteins coming from the first dimension column, before their selective elution in the second dimension column. A protein standard mixture of bovine serum albumin, β-lactoglobulin and glucose oxidase was used to optimize the gradient chromatographic separation conditions, after evaluating their retention behavior in each single column. Finally, the optimized 2D-LC method was applied to the protein analysis in eggs, infant milk powder and soy flour samples.

References
1. L.I. Tsonev, A.G. Hirsh Journal of Chromatography A, 1468 (2016) 173–182.
2. B. Ji, B. Xia, J. Liu, Y. Gao, L. Ding, Y. Zhou. Journal of Chromatography A, 1466 (2016) 199–204.
3. G. Guiochon, N. Marchetti, K. Mriziq, R.A. Shalliker. Journal of Chromatography A, 1189 (2008) 109–168.

The Extractor Naviglio® in Food Productions

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For over a decade the Naviglio Extractor is a good alternative to solid-liquid extraction techniques such as maceration and percolation, as has been amply demonstrated that it is able to provide the same quality (if not more) of the extracts obtained with the traditional extraction techniques, also provides additional benefits such as significant reduction in the time of the extraction process (Ten days of maceration extraction equals one hour of extraction by the Naviglio extractor equal conditions) and a more efficient extraction. The principle on which it bases its functioning (Naviglio's Principle) is studied in graduate courses in Herbal Techniques of several Italian universities. Currently, the Naviglio extractor is widely used in many fields of research and production (herbal, nutritional supplements, homeopatics, cosmetics, beverages). In the food sector, in particular, the Naviglio Extractor has been shown to be a viable alternative to macerate for: production of lemon liquor (limoncello) and similar liquors; and production of bitter elixir of juniper; rapid aging of wines, brandies and liqueurs; extraction of lycopene from tomato processing waste. Finally, have recently been found more unconventional applications of the Naviglio extractor as the rapid hydration of dried vegetables and their simultaneous aromatization, cleaning washers for the production of cork stoppers, cleaning the rubber polymer, the tanning of leather. In Figure 1 laboratory prototype was showed.

NAVIGLIO'S PRINCIPLE: The generation of a negative pressure gradient, using a suitable solvent, between the outside and inside of a solid matrix containing the material to be extracted, followed by a sudden reinstatement of the initial balanced conditions, leads to the forced extraction of those compounds that are not chemically linked to the main structure making up the solid.

FIGURE 1. Laboratory prototype of Esxtractor Naviglio (1998).

Reference
1. Naviglio, D. Naviglio's Principle and presentation of an innovative solid-liquid extraction technology: Extractor Naviglio®. Analytical Letter, 2003. 36(8):1647-1659.

First profiling of flavonoids in Tarocco "Lempso" (*Citrus Sinensis* L. Osbeck) clone variety and its antioxidant potential by DPPH-UHPLC-PDA-IT-TOF

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Clonal selection and hybridization are valid strategies to obtain fruits with enhanced sensorial and nutraceutical properties[1,2]. Within *Citrus sinensis* varieties, Tarocco clone "Lempso" is a typical product of Calabria region (Italy) characterized from a red pulp. This is the first report concerning its accurate profiling.

To characterize in detail the flavonoid composition of Lempso clone and to compare its antioxidant potential with other Citrus varieties by a fast screening method, extracts were subjected to solid phase extraction and the quali/quantitative profile was elucidated through ultra high performance liquid chromatography (UHPLC) coupled to photodiode array (PDA) and ion trap-time of flight (IT-TOF) mass spectrometry detection, and compared to both Cleopatra mandarin (*Citrus reticulata*) and blood orange (*Citrus sinensis* (L.) Osbeck) Sanguinello varieties. The antioxidant activity was assessed by pre-column DPPH reaction coupled to UHPLC-PDA[3].

Lempso is characterized by flavonoids and anthocyanins. Flavanones content (Hesperidin: 57.19 ± 0.49, Vicenin-2: 4.59 ± 0.03, Narirutin: 5.78 ± 0.13 mg/100 mL) was considerably higher than Cleopatra and Sanguinello varieties. The developed DPPH-UHPLC-PDA method provides information regarding the single contributions to antioxidant activity, highlighting how Ferulic acid, Quercetin and Cyanidin derivatives possess considerable radical scavenging activity (> 50%)[4,5]. The total antioxidant activity was also evaluated and compared with positive controls, showing higher scavenging activity than Cleopatra and Sanguinello (IC50: 333.76 ± 10.81 μg/mL vs 452.62 ± 10.81 and 568.39 ± 26.98 μg/mL, respectively).

These data evidence the nutraceutical potential of Lempso variety, which could be an ingredient for functional beverages.

References

1. Bretó MP, Ruiz C, Pina JA, Asíns MJ. 2001. The diversification of Citrus clementina Hort. ex Tan., a vegetatively propagated crop species. Mol Phylogenet Evol. 21: 285–293.
2. Rapisarda P, Fabroni S, Peterek S, Russo G, Mock HP. 2009. Juice of New citrus hybrids (Citrus clementina Hort. ex Tan.× C. sinensis L. Osbeck) as a source of natural antioxidants. Food Chem. 117: 212–218.
3. Sommella E, Pepe G, Pagano F, Conte G, Carimi F, Tenore GC, Novellino E, Manfra M, Russo M, Campiglia P. 2016. Rapid Screening of Antioxidant Anthocyanins in Autochthonous Nero d'Avola Grape Clones by Pre-column DPPH Reaction Coupled to UHPLC-UV/Vis-IT-TOF: a Strategy to Combine Chemical data and Genetic Diversity. Food Anal Method. 10: 2780-2790.
4. Kanski J, Aksenova M, Stoyanova A, Butterfield DA. 2002. Ferulic acid antioxidant protection against hydroxyl and peroxyl radical oxidation in synaptosomal and neuronal cell culture systems in vitro: structure–activity studies. J Nutr Biochem. 13: 273–281.
5. Stintzing FC, Stintzing AS, Carle R, Frei B, Wrolstad RE. 2002. Color and antioxidant properties of cyanidin-based anthocyanin pigments. J Agric Food Chem. 50: 6172–6181.

High Temperature Liquid Chromatography for Lipid Analysis.

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Lipidomics is an emerging field where new analytical techniques are playing an important role for instance in the biomedical research having a wide range of applications in drug and biomarker development [1]. Since the lipids have a large chemical diversity the analysis is characterized by a variety of analytical challenges, above all the solubility issue and the structure similarity within the lipid classes [2]. Porous graphitic carbon (PGC) is a stationary phase with unique chromatographic behavior showing strong retention of both non-polar and polar compounds, the first due to the contribution of the dispersive interactions and the latter due to the interaction with the planar polarizable graphitic surface. The PGC is a suitable stationary for high temperature liquid chromatography (HTLC) since it is resistant to extreme conditions in pH and temperature [3-4]. The retention behavior on reversed phase stationary phases can be predicted using a partial least square modeling (PLS) of structural features combined with chromatographic parameters [5]. A similar approach was used for modelling of retention factors on PGC using chromatographic conditions (temperature, toluene and additive concentration), the structural elements of the compounds (e.g. molecular weight, total carbons and sp2-hybridized carbon), including square and interaction effects. The multivariate regression shows a coefficient of determination (R2) 0.961 for the reference values and 0.948 for the predicted values. The model has been built using the evaporative light scattering detector (ELSD) with chromatographic conditions suitable for mass spectrometry detection. This approach helps to understand the chromatographic behavior exploiting the temperature as a “third chromatographic dimension“. Based on the results, a methodology for the analysis of phospholipids based on gradient elution and tandem mass spectrometric detection is suggested

References
[1] M.R. Wenk, Nat Rev Drug Discov. 4 (2005) 594–610.
[2] E. Fahy, J. Lipid Res. 50 (2009) S9–S14.
[3] S. Heinisch, Journal of Chromatography A. 1216 (2009) 642–658
[4] L. Pereira, J. of Liquid Chromatography & Related Technologies. 31 (2008) 1687–1731.
[5] P. Olsson, Journal of Chromatography A. 1360 (2014) 39–46

New modified coated carbon fiber as solid phase for microextraction and in-situ derivatization of phytohormones in real samples.

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Phytohormones play a vital role in plant growth and metabolic processes[1]. As a minor component of the metabolome, phytohormones are of particular significance due to their role in the regulation of germination, growth, reproduction, and the protective responses of plants against stress. In fact, they control the balanced response of plants to adverse environmental conditions or biological threats. Thus, the simultaneous quantitative profiling of different classes of phytohormones provides a useful basis for defining additive, synergistic or antagonistic hormonal activities in biofertilizers or natural compounds. Phytohormones are typically present at trace levels in biological matrices, and the coexistence of a wide variety of interferents make their analysis rather challenging[2]. In this work, an integrated sample pre-treatment and derivatization method based on a new coated carbon fiber microextraction that allows a rapid extraction, separation, and highly sensitive phytohormone detection has been realized and characterized. Carbon fibers, chosen as substrate for their excellent high thermal and chemical stabilities, high porosity, and low cost, were chemically modified to obtain new surface characteristics in terms of polarity and adsorbing capacities. Three phytohormones (jasmonic acid, indole-3-acetic acid and abscisic acid) were simultaneously extracted, in-situ derivatized with N,O-bis(trimethylsilyl)trifluroacetamide and directly subjected to analysis by gas chromatography–mass spectrometry. The developed method allowed in few step and short time low detection limits (0.62 – 3.72 ng mL^{-1}), good linearity (in the range 3.0 – 5000 ng mL^{-1}) and recoveries (81.6 to 105.8%). Furthermore, enrichment response factors (calculated as the ratio of peak areas obtained by SPME thermal desorption and direct injection) up to 3200, high derivatization rates ($\geq$ 90%) and good reproducibility (RSD $\leq$ 20% at 50 ng mL-1) were obtained. The developed method was applied for the evaluation of phytohormone concentration in blended tomato samples.

References
1. B.D. Cai, J. Yin, Y.H. Hao, Y.N. Li, B.F. Yuan, Y.Q. Feng, J Chromatogr A, 1406 (2015) 78-86.
2. H. Zhang, S.N. Tan, C.H. Teo, Y.R. Yew, L. Ge, X. Chen, J.W. Yong, Talanta, 139 (2015) 189-197.

A high throughput mass spectrometry screening analysis based on two-dimensional carbon microfiber fractionation system

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Compounds identification and quantification in complex samples are still a great challenge[1,2], because real matrices are generally constituted by an impressive number of substances, which shows great differences in physical and chemical properties, requiring then complex pretreatment, separation and analysis procedures[3]. In particular, polarity plays a great role in this perspective, making their simultaneous detection and quantification very demanding. Another critical issue that should be addressed is the great difference in the substance content (from mg g^{-1} to ng g^{-1}), that can lead to mask trace compounds or to saturate the limited capacity of the separation columns: most of them remain unknown or not revealed[4]. A quite interesting case-of-study in this field is the analysis of medicinal plant extracts. Their composition can provide very important information in metabolomics studies, in the comprehension of the synergistic effects of major and minor components for the plant resources exploitation and for the knowledge of therapeutic mechanisms[1,4]. The high complexity of these extracts, containing both polar, medium polar and non-polar substances lead to very complex, tedious and time-consuming analytical procedures for their analyses. One possible solution to overtaking all these drawbacks can rely on a new analytical approach that gathers a pretreatment that split molecules with different polarities in distinct fractions with direct MS analyses[5]. Our research has been focused then toward the realization of a system that could allow this separation in a fast, reliable and inexpensive way. A novel high-throughput, solvent saving and versatile integrated two-dimensional microscale carbon fiber/active carbon fiber system (2DμCFs), that allows a simply and rapid separation of compounds in low-polar, medium-polar and high-polar fractions, has been coupled with ambient ionization-mass spectrometry (ESI-Q-TOF-MS and ESI-QqQ-MS) for screening and quantitative analyses of real samples. 2DμCFs led to a substantial interference reduction and minimization of ionization suppression effects, thus increasing the sensitivity and the screening capabilities of the subsequent MS analysis. The method has been applied to the analysis of *Schisandra Chinensis* extracts, obtaining with a single injection, a simultaneous determination of 33 compounds presenting different polarities, such as organic acids, lignans, and flavonoids in less than 7 min, at low pressures and using small solvent amounts. The method was also validated using 10 model compounds, giving limit of detections (LODs) ranging from 0.3 to 30 ng mL^{-1}, satisfactory recoveries (from 75.8 to 93.2%) and reproducibilities (relative standard deviations, RSDs, from1.40 to 8.06%).

References
1. Z. Li, S. Xiao, N. Ai, K. Luo, X. Fan, Y. Cheng, , J.Chromatogr. A 1376 (2015) 126–142.
2. J. Shen, X. Mo, Y. Tang, L. Zhang, H. Pang, Y. Qian, Y. Chen, W. Tao, S. Guo, E. Shang, S. Zhu, Y. Ding, J. Guo, P. Liu, S. Su, D. Qian, J.A. Duan, J. Chromatogr. A 1297 (2013) 168–178.
3. H. Fu, W. Fu, M. Sun, Q. Shou, Y. Zhai, H. Cheng, L. Teng, X. Mou, Y. Li, S. Wan, S. Zhang, Q. Xu, X. Zhang, J. Wang, J. Zhu, X. Wang, X. Xu, G. Lv, L. Jin, W. Guo, Y. Ke, Anal. Chem. 83 (2011) 6518–6526.
4. J.L. Cao, J.C. Wei, M.W. Chen, H.X. Su, J.B. Wan, Y.T. Wang, P. Li, J. Chromatogr. A 1371 (2014) 1–14.
5. S. Ahmad, M. Tucker, N. Spooner, D. Murnane, U. Gerhard, Anal. Chem. 87 (2015)754–759.

Preparation of Nanoemulsions From Peel Extracts Of Citrus Fruit Obtained By Rapid Solid Liquid Dynamic Extraction (RSLDE)

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Citrus fruits are a source of several characteristic compounds which are responsible for their odour and biological proprieties.

To be more detailed, extracts of citrus fruit peels may show antimicrobial, anti-inflammatory and haemostatic activities which are due to a number of inorganic compounds (e.g., phosphorus, calcium, copper), essential oils (e.g., terpenes), fibers, vitamins and fats.

So much so that they have several applications in the perfume and cosmetics industry as well as in the food, beverage and confectionary industries as flavouring agents for liqueurs, teas, candies and soft drinks.

However, the final properties of the citrus fruit peels crude extracts strongly depend on the details of the extraction process.

Cold pressing and hydrodistillation are presently the most used techniques employed in the production of fruit peels extracts which, however, contain mainly essential oils.

Here we present results on the composition of citrus fruit peels extracts obtained by a very performing and inexpensive extraction technology based on Rapid Solid Liquid Dynamic Extraction (RSLDE) implemented via an automated apparatus (Naviglio Extractor).

Interestingly, both volatile and non-volatile components were detected in crude extracts characterized mainly via GC/MS analysis.

Then, very stable ultra-small oil in water emulsions (with oil droplets less than 20 nm in diameter) have been produced by combining RSLDE with emulsification of extracts by a high-pressure homogenizer. Additionally, the oil is under investigations in terms of bioactivity.

This is an intriguing aspect of our investigations because of the potentialities of these oils in the field of biotechnology due to their therapeutic activities. Indeed, attempts to prepare emulsions from similar commercial oils obtained with usual extraction methods resulted unsatisfactory.

MSPD Extraction And UHPLC-ESI-MS/MS Characterization Of Selected Phenolic Acids And Flavonoids

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Matrix solid phase dispersion (MSPD) is an extraction method that allows in few steps the extraction/isolation of a widespread range of molecules, with limited sample and lower solvent quantities consumption (1). In this technique, the investigated sample is blended with a chemically derivatized solid support; the resulted mixture is packed in a cartridge next subjected to a washing and an elution steps. Thanks to hydrophobic and hydrophilic interactions that occur, in these steps the interference removal and the extraction/isolation of the target analytes are obtained. This technique can be applied to complex matrices and to any target analyte[2].

In the whole of the different fields in which MSPD can be applied, we focused our attention to plant polyphenolic compounds (PCs). These molecules are secondary metabolites with different structures and functions. Among them, we selected phenolic acids and flavonoids classes, which have already displayed interesting biological properties in human health[3].

The optimization of the MPSD different steps and conditions was performed on different silica based sorbents (C2, C8, C18E-capped, C18T-uncapped, phenyl) and 16 selected analytes with different polarity and representatives of the subclasses of which they belong. The MSPD procedure was followed by an UHPLC-ESI-MS/MS analysis.

The most suitable MSPD protocol turned out to be the following: C18-T as bonded phase, 1 mL of 90:10 water/methanol solution for the washing step and an elution step with 500µL of methanol. After the preliminary results, the method was successfully implemented with a 35analytes of the same selected classes.

The method was also applied to *Ocimum basilicum*, the common basil worldwide used in food flavoring. The obtained results present good analytical performances in terms of repeatability, accuracy, linearity and matrix effect.

The optimized MSPD-LC-MS/MS method can be adapted to similar matrices and could provide a valid basis for additional or similar investigations of other plant bioactive compounds.

References
1. S.A. Barker, A.R. Long, C.R. Short. “Isolation of drug residues from tissues by solid phase dispersion”; *J. Chromatogr. A*, 1989, *475*, 353–361.
2. S.A. Barker; “Matrix solid phase dispersion (MSPD)”; *J. Biochem. Biophys. Methods*, 2007, *70*, 162 2007.
3. Pandey K.B., Rizvi S.I.; “Plant polyphenols as dietary antioxidants in human health and disease”; *Oxidative Medicine and Cellular Longevity*, 2(5), 270-278.

Investigation on the Role of Carbohydrate Moiety in the Catalytic Activity of a Laccase from Trametes Versicolor

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Laccases (EC 1.10.3.2) are polyphenol oxidases able to catalyze the oxidation of various organic and inorganic compounds with the concomitant four-electron reduction of molecular oxygen to water. Typical substrates are particularly those with electron-donating groups such as phenols (−OH) and anilines (−NH_2). An important feature of this kind of biomolecule is the high level of glycosylation, with covalently linked carbohydrate moieties ranging from 10-50% of the total weight, which may contribute to the high stability of the enzyme[1]. The oxidation of carbohydrate residues by periodate is a common strategy for the site-specific modification/immobilization of antibodies in order to apply them in various bioanalytical methods. According to this approach, diols located in the carbohydrate chains are cleaved by periodate to form reactive aldehyde groups or hydrazide residues[2]. In the present study, the possibility of improving the immobilization yields of a Trametes versicolor laccase on chitosan *via* the same oxidation protocol is proposed, in order to explore the role of carbohydrate moiety through the modification of monosaccharides covalently attached to the enzyme. As a matter of fact, the immobilization of enzymes has been usually accomplished by several procedures, most of which include the covalent attachment of the enzymes to various matrices through a cross linking agent[3]. In this work laccase was submitted to undergo periodate oxidation and, after the elimination of the remaining periodate through a dialysis step, the oxidized glycoprotein is directly incubated with chitosan macro particles. The buffer favourable conditions and the optimal laccase concentration for the immobilization were investigated as well as the aldehyde groups formed after the oxidation were qualitatively and quantitatively determined through 2,4-dinitrophenylhydrazine spectrophotometric assay[4]. The bioreactor was then characterized for kinetic parameters (Michaelis-Menten constant and maximum rate), reuse, storage stability and pH/temperature profiles. The study of the best operative conditions is useful for the application of the biocatalysts in several biotechnological processes. The oxidation procedure has been proved to be feasible for the preparation of stabilized glycoproteins without the introduction of foreign molecules suggesting that the carbohydrate moiety of laccase, involved in the interaction with ammoniac groups of chitosan, doesn't appear to be closely related with the catalytic site of the protein.

References
1. Kunamneni A., Plou F.J., Ballesteros A., Alcade M., "Laccases and Their Applications: A Patent Review"; *Recent Patents on Biotechnology 2*, 2008, 10-24.
2. Carrie A.C. Wolfe and David S. Hage, "Studies on the rate and control of Antibody Oxidation by Periodate"; *Analytical Biochemistry*, 1995, *231*, 123-130.
3. Sheldon R.A. and S. Van Pelt, "Enzyme immobilization in biocatalysis: why, what and how"; *Chem. Soc. Rev.*, 2013, *42*, 6223-6235.
4. Mesquita C.S., Oliveira R., Bento F., Geraldo D., Rodrigues J.V., Marcos J.C., "Simplified 2,4-dinitrophenylhydrazine spectrophotometric assay for quantification of carbonyls in oxidized proteins"; *Anal. Biochem.*, 2014, *458*, 69-71.

Monitoring peptides released after gastro-intestinal digestion by online comprehensive LC × UHPLC-HRMS: A case study on buffalo milk dairy products

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Dairy products contain many bioactive peptides that are encrypted in the sequence of precursor proteins and become bioaccessible and active after release during gastro-intestinal digestion[1]. The resulting matrix are often very complex, containing hundreds of compounds. Conventional analytical techniques based on monodimensional liquid chromatography methods coupled to mass spectrometry are not capable to handle this challenging samples and thus high peak capacity values are necessary[2]. In this regard, we developed an online comprehensive two-dimensional liquid chromatography platform by two coupling two reversed phase columns operating at different pH values[3]. In the first dimension, a microbore RP column was employed whereas in the second dimension two different short sub-2 μm stationary phases were compared: a fully porous monodisperse C18 column and a core-shell C18 column[4]. The peptides were monitored by UV detection and identified by tandem mass spectrometry (MS/MS). The developed method provided double peak capacity values with respect to monodimensional methods and high orthogonality, together with a major number of identified peptides and a quick visualization of matrix differences by 2D map comparison. The method is highly suitable for peptidomics studies[5].

References
1. H. Korhonen, A. Pihlanto, "Bioactive peptides: production and functionality"; *Int. Dairy J.*, 2006, *16*, 945-960.
2. B. Hernández-Ledesma, L. Amigo, M. Ramos, I. Recio, "Application of highperformance liquid chromatography–tandem mass spectrometry to the identification of biologically active peptides produced by milk fermentation and simulated gastrointestinal digestion"; *J. Chromatogr.*, 2004, *17*, 107-114.
3. P. Donato, F. Cacciola, E. Sommella, C. Fanali, L. Dugo, M. Dachà, P. Campiglia, E. Novellino, P. Dugo, L. Mondello, "Online comprehensive RPLC × RPLC with mass spectrometry detection for the analysis of proteome samples"; *Anal. Chem.*, 2011, *83*, 2485-2491.
4. E. Sommella, G. Pepe, G. Ventre, F. Pagano, M. Manfra, G. Pierri, O. Ismail, A. Ciogli, P. Campiglia, "Evaluation of two sub-2 μm stationary phases, core–shell and totally porous monodisperse, in the second dimension of on-line comprehensive two-dimensional liquid chromatography, a case study: separation of milk peptides after expiration date", *J. Chromatogr. A*; 2015, *1375*, 54-61.
5. J.N. Fairchild, M.J. Walworth, K. Horvátha, G. Guiochon, "Correlation between peak capacity and protein sequence coverage in proteomics analysis by liquid chromatography–mass spectrometry/mass spectrometry"; *J. Chromatogr. A*, 2010, *1217*, 4779-4783.

Dried Blood Spot analysis for therapeutic drug monitoring: determination of ibuprofen, uric acid and creatinine by UHPLC-MS/MS

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The aim of this work was to develop an innovative UHPLC-MS/MS method for the determination of ibuprofen, creatinine and uric acid in dried blood spots (DBS) collected from preterm infants with Patent Ductus Arteriosus (PDA). PDA represents a hot topic in neonatology, whose pathophysiology, diagnosis and management are still a debated issue. Ductal patency is primarily due to an increased oxygen tension and high prostaglandin-E_2 (PGE_2) levels, which are suppressed by cyclooxygenase inhibitors (e.g. ibuprofen). The choice of treatment is challenging as it depends on a complex risks/benefits analysis due to frequent failures and severe adverse effects of drug (e.g. impaired renal function and intestinal perforation). The present approach can be a potential tool for the non-invasive, rapid, and painless monitoring of ibuprofen treatment and its main pathophysiologic effects on the kidney of preterm infants suffering from PDA. The analytical procedure combines a fast and reliable extraction of the analytes from a single drop of blood and a highly sensitive and selective UHPLC-MS/MS technique. Whole blood (20 µL) was spotted onto a filter paper, dried, and then extracted and diluted with mobile phase prior to analysis. The sampling and extraction steps were optimized by testing two types of sample collection cards, (i.e. Whatman FTA DMPK-B and Whatman-903), and various water/methanol mixtures. The analytical figures of merit, i.e. linearity, detection and quantification limits, intra- and inter-day precision and recovery, are finally discussed.

Individual and Cyclic Estrogenic Profile in Woman: Structure and Variability of the Data

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Women of childbearing are the ones who still have the period, thus the amount of estrogens, produced by the ovaries, results cyclic with wide fluctuations throughout the menstrual cycle.
To date, the variations of the principal estrogens (estradiol, estrone and estriol) were only evaluated, consequently the aim of the study was to examine in depth the cyclic fluctuations of some metabolites.
A Gas Chromatography coupled to Mass Spectrometry (GC-MS) method capable of detecting estradiol, estrone, estriol and their metabolites in urine was developed, based on an experimental design, and fully validated.
The following validation parameters were investigated according to ISO 17025 requirements: linearity range, selectivity, specificity, limit of detection (LOD), limit of quantitation (LOQ), trueness, intra- and inter-assay precision, repeatability, matrix effect, extraction recovery and carry-over.
A wide panel of estrogens, consisting of 17α-estradiol, 17β-estradiol, estrone, estriol, 4-methoxyestrone, 2-methoxyestrone, 16α-hydroxyestrone, 4-hydroxyestrone, 2-hydroxyestrone, 4-methoxyestradiol, 2-methoxyestradiol, 4-hydroxyestradiol, 2-hydroxyestradiol, 16-epiestriol and 17-epiestriol, was monitored in some young healthy women throughout a complete menstrual cycle.
The resulting data were simultaneously evaluated through the application of the Parallel Factory Analysis (PARAFAC) method, in order to explore the variability of each analyte and each class of estrogens.
The estrogens, furthermore, play a significant role in the development of ovarian and breast tumors. In fact, these carcinomas are closely related to the alteration of the estrogenic production.
Urine samples, collected from healthy post-menopausal women and volunteers affected by breast cancer, were analysed.
Post-menopausal women were chosen because of the higher incidence of these tumors and the greater stability of the urinary estrogenic concentration compared to young women.
The evaluation of the estrogenic profile was performed and the resulting data were analysed by multivariate statistic techniques. Among the most important techniques, Discriminant Analysis (DA), Partial Least Square – Discriminant Analysis (PLS – DA), Principal Component Analysis (PCA), Cluster Analysis and Soft Independent Models of Class Analogy (SIMCA), were tested in order to discriminate between healthy women and the ones suffering from carcinomas.

Phospholipid profiling of donkey milk by HILIC with electrospray ionization and Fourier-transform high resolution/accuracy mass spectrometry

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Bovine milk represents an important source of essential nutrients which contribute to the growth and development of newborns when breast feeding cannot be provided. Unfortunately, approximately 2–3% of infants younger than one year have reported allergy to cow milk[1]. Many clinical researches have demonstrated that donkey milk can be considered a potential alternative to cow milk intolerant infants due to its very similar composition to human milk[2]. For this reason, several studies have been focused on the proteome[3] and peptidome[4] characterization of donkey milk. As far the lipid fraction is concerned, a number of authors investigated triglyceride (TAG)[5] and fatty acid composition[6] showing that, like human milk, TAG C52 was the most abundant; saturated fatty acids, predominantly palmitic acid, were present mainly in the *sn-2* position of the glycerol backbone[5]. To our knowledge, few data are accessible on the minor polar lipid species of donkey milk fat as phospholipids (PL)[7,8]. The aim of this study was to characterize these minor lipids on a pool of samples of donkey milk collected from Martina Franca breed. Phospholipid classes were separated based on the polarity of their headgroups using hydrophilic interaction liquid chromatography (HILIC) by gradient elution with acetonitrile and water containing formic acid and ammonium acetate as mobile phase. A solid-core 2.6 µm HILIC column was employed at a flow rate of 0.3 mL/min at ambient temperature. Structural characterization of PLs was performed by electrospray ionization with high-resolution/accuracy Fourier-transform Orbitrap mass spectrometry (ESI-FTMS) and tandem MS. For a complete depiction of as many as possible PL molecular species, the analyses were performed in positive, negative and negative with in source fragmentation ion mode. Indeed, in the last modality a higher number of product ions were attained in MS/MS analyses of phosphatidylcholines (PC) and sphingomyelins allowing a more confident characterization. It was found that phosphatidylethanolamines, phosphatidylcholines and sphingomyelins were the most abundant PL, followed by phosphatidylinositols, lysophosphatidylethanolamines, and lyphosphatidylcholines. Besides, the presence of hexosylceramides, gangliosides and N-acetylphosphatidylethanolamines was assesses for the first time in donkey milk.

References
1. Restani P. et al., Ann Allergy Asthma Immunol 89 (2002) 11–15
2. Claeys, W.L. et al., Food Control 42 (2014) 188–201.
3. Gallina S. etal., Amino Acids 48 (2016) 2799–2808
4. Piovesana S. et al., J Proteomics 119 (2015) 21-29.
5. Chiofalo, B. et al., Immunopharmacol. Immunotoxicol. 33 (2011) 633–644.
6. Salimei, E. et al., Anim. Res. 53 (2004) 67–78.
7. Donato, P. et al., J. Chromatogr. A 1218 (2011) 6476–6482.
8. Zou, X. et al., J. Agric. Food Chem. 61 (2013) 7070–7080.

Label free shotgun proteomics approach to characterize muscle tissue from farmed and wild european sea bass (Dicentrarchus labrax)

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Recently, aquaculture has become central to meet the increased fish demand; according to the Organization for Economic Cooperation and Development (OECD) and to the Food and Agriculture Organization (FAO), in 2022 the world aquafarming will be increased by a 35% factor, while traditional fishing only by 5%, due to population growth, rising incomes and increasing urbanisation[1]. During farming, fish species are subjected to a plethora of stimuli and environmental constraints such as different diet, feeding regiments, crowding, different water quality (temperature, salinity), with respect to wild fish species. The nutritional characterization of aquaculture products represents an important step toward a quality certification process of seafood that informs the consumer about the origin, handling practices, and processing history of the products, thus guaranteeing safety requirements and nutritional properties[2]. Under a nutritional perspective, studies on fatty acid and lipid compositions between wild and aqua-farmed individuals have been playing a major role in the past years leading to the publication of many papers in the literature, which highlight that omega-3 fatty acids were naturally more concentrated in wild fish, whereas their presence in farmed fish was lower in favor of omega-6 and oleic acid, as an evident consequence of food supplementation[3]. In the last years the study of protein content has also become particularly important for the characterization of food products and to assess food quality and safety[4]. Proteomics can be exploited for sea food as well, in order to distinguish fish species, trace their origin and compare the farmed product to the wild one. Differences may thus be expected. In this study, a proteomic profile of farmed and wild sea bass samples was performed, employing a fractionation strategy where peptide samples were first separated by high-pH RP and then by low-pH RP chromatography. The peptides were finally analyzed by a typical shotgun proteomics workflow with high resolution tandem MS and label free quantitative analysis. The chosen fractionation approach was successful, with 70% of the identified peptides detected in a single fraction. This allowed to greatly improve the fish muscle protein characterization and detect some interesting differences between wild fish and farmed sea bass. 69 proteins were overexpressed in farmed fish samples, whereas 182 proteins were underexpressed. Some of these proteins could be related to the breeding conditions and the diet with which fishes were fed, thus providing some interesting results for assessing food quality based on a comprehensive proteomic study.

References

1. Food and Agriculture Organization of the United Nations; "The State of World Fisheries and Aquaculture"; 2016; http://www.fao.org/3/a-i3720e.pdf.
2. M.F. Addis, Farmed and Wild Fish, in: F. Toldrá, L.M.L. Nollet (Eds.), Proteomics in Foods, Springer US, Boston, MA, 2013: pp. 181–203.
3. R. Costa, A. Albergamo, M. Piparo, G. Zaccone, G. Capillo, A. Manganaro, P. Dugo, L. Mondello, "Multidimensional gas chromatographic techniques applied to the analysis of lipids from wild-caught and farmed marine species", *Eur. J. Lipid Sci. Technol.*, 2017, *119*, 1600043.

A.L. Capriotti, C. Cavaliere, S. Piovesana, R. Samperi, A. Laganà; "Recent trends in the analysis of bioactive peptides in milk and dairy products"; *Anal. Bioanal. Chem.*, 2016, 1–9.

A rapid microextraction by packed sorbent - liquid chromatography tandem mass spectrometry method for the determination of dexamethasone disodium phosphate and dexamethasone in aqueous humor of patients with uveitis

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Uveitis, i.e. inflammatory disorders of the uveal tract of the eye, represent a particular burden of disease during adulthood and frequently cause cataract formation. Supplementation with corticosteroids is usually recommended as perioperative prophylaxis in cataract surgery. In particular, in topical ophthalmic products, the dexamethasone disodium phosphate (DEX-SP), a glucocorticoid that can be hydrolyzed to free desamethasone (DEX) by phosphatase, is one of the most prescribed worldwide to treat ocular inflammations. The topical administration of this drug still remains ideally preferable, however its major drawback lies in its poor permeability towards the corneal epithelium (less than 3% of the instilled dose reaches the aqueous humor)[1].

The analysis of dexamethasone and dexamethasone sodium phosphate in aqueous humor requires high sensitivity and selectivity due to the presence of these compounds at low concentration levels. Another drawback lies in the low amount of biological sample that can be collected during surgery. In this context, we developed and validated a new method based on microextration by packed sorbent (MEPS) coupled with liquid chromatography-tandem mass spectrometry (LC-MS/MS) for the determination of DEX and DEX-SP in human aqueous humor with the final goal of evaluating the effectiveness of the glucocorticoid topic administration. In a research program aimed to the development of extraction methods for rapid, sensitive and high-throughput MS-based analysis[2], the use of MEPS was proposed as miniaturized extraction technique, since it permits to combine sample processing, concentration and clean-up into a fully-automated online sampling/injecting device and to process reduced sample volume[3]. A central composite design and the multicriteria method of the desirability functions were applied for optimization of MEPS conditions allowing to find the best conditions for the simultaneous extraction of both the analytes. Detection was performed on a LTQ XL linear ion trap mass spectrometer using electrospray ionization in positive ion multiple reaction monitoring mode. Validation of the assay showed quantitation limits of 0.7 and 0.5 µg/L for DEX-SP and DEX, respectively, a very good precision (RSD $\leq$ 16%) and recovery rates in the 91 – 119% range[4]. The method also demonstrated rapid analysis time, low volume consumption and good selectivity, thus being a valuable tool for clinical studies to assess the reliability of dexamethasone administration in patients affected by uveitis.

References
1. J.R. Villanueva, L.R. Villanueva, M.G. Navarro, Int. J. Pharm. 516 (2017) 342–351.
2. M. Mattarozzi, M. Milioli, F. Bianchi, A. Cavazza, S. Pigozzi, A. Milandri, M. Careri, Food Control 60 (2016) 138–145.
3. F. Bianchi, M. Mattarozzi, N. Riboni, P. Mora, S. A. Gandolfi, M. Careri, J. Pharm. Biomed. Anal. submitted for publication.
4. Guidance for Industry, Bioanalytical Method Validation, US Department of Health and Human Services, Food and Drug Administration, 2001 https://www.fda.gov/downloads/Drugs/Guidances/ucm368107.pdf (accessed 05.04.2017).

In silico **modeling tools for the overproduction of molecules with a biotechnological interest: experimental validation of model predictions on** ***Streptomyces ambofaciens***

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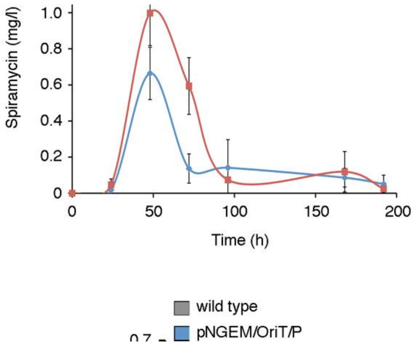
Both academic and industrial laboratories currently use constraint-based reconstruction methods to predict optimal genetic modifications aiming at improving the yield of chemical production[1]. *Streptomyces ambofaciens*, a prolific producer of bioactive compounds has been studied with different modeling tools[2]. The interest is linked to its ability to produce a wide range of secondary metabolites such as spiramycin, kinamycin, antimycin and stambomycins, and novel polyketides with antibacterial and antiproliferative activities[3]. In this study, the metabolic pattern of *Streptomyces ambofaciens* has been globally explored: a set of candidate overexpression gene targets supposed to lead to spiramycin overproduction have been evidenced through metabolic modeling. Model predictions were experimentally validated by genetic manipulation of the ethylmalonyl-CoA metabolic node, providing evidence that spiramycin productivity may be increased by enhancing the carbon flow through this pathway. The goal was achieved by over-expressing the *ccr* paralog *srm4* in an *ad hoc* engineered plasmid. The first metabolic reconstruction of *S. ambofaciens* and the successful experimental validation of model predictions have been described and the validity and the importance of *in silico* modeling tools for the overproduction of molecules with a biotechnological interest demonstrated. As a result, the proposed metabolic reconstruction represents a solid platform for the future exploitation of *S. ambofaciens* biotechnological potential[4].



References
1. King, Z. A., Lloyd, C. J., Feist, A. M., and Palsson, B. O. (2015). Next-generation genome-scale models for metabolic engineering. *Curr. Opin. Biotechnol.* 35, 23–29. doi: 10.1016/j.copbio.2014.12.016.
2. Baltz, R. H. (2016). Genetic manipulation of secondary metabolite biosynthesis for improved production in *Streptomyces* and other actinomycetes. *J. Ind. Microbiol. Biotechnol.* 43, 343–370. doi: 10.1007/s10295-015-1682-x.
3. Thibessard, A., Haas, D., Gerbaud, C., Aigle, B., Lautru, S., Pernodet, J. L., et al. (2015). Complete genome sequence of *Streptomyces ambofaciens* ATCC 23877, the spiramycin producer. *J. Biotechnol.* 214, 117–118. doi: 10.1016/j.jbiotec. 2015.09.020
4. Fondi M, Pinatel E, Talà A, Damiano F, Consolandi C, Mattorre B, Fico D, Testini M, De Benedetto GE, Siculella L, De Bellis G, Alifano P and Peano C (2017) Time-Resolved Transcriptomics and Constraint-Based Modeling Identify System-Level Metabolic Features and Overexpression Targets to Increase Spiramycin Production in *Streptomyces ambofaciens*. *Front. Microbiol*. 8:835. doi: 10.3389/fmicb.2017.00835.

A promising approach to early detect Sickle Cell Anemia

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Sickle Cell Anemia (SCA) is the most common inherited hemoglobin disorder, associated with recurrent painful episodes, ongoing hemolytic anemia and progressive multi-organ damage. It is so defined because it imparts to the red blood cells (RBCs) a sickle shape. SCA is caused by the presence of an abnormal hemoglobin where the glutammic acid is replaced by the valine in the β chain, leading to the formation of hemoglobin S (HbS)[1].

The clinical overview is very heterogeneous and it is characterized by chronic hemolysis and vaso-occlusion due to the polymerization of HbS into the RBCs[2].

A multidisciplinary approach to diagnosis of sickle cell disease is usually required and often it is a problem, especially in countries where the resources are scarce or absent. To develop quick and effective method for a preliminary detection of hemolytic anemia has been become very important.

Based on previous results achieved for the β-Thalassemia syndromes, the coupling of Thermogravimetric Analysis (TGA) and chemometrics was investigated to develop a model of prediction for Sickle Cell Anemia[3].

Whole blood samples from healthy subjects and falcemic subjects have been investigated by Thermogravimetric Analysis and the resulting TG and DTG curves were considered for the chemometric analysis to identify a characteristic thermal behavior among the two populations according to a different amount of water content and corpuscular fraction.

The same samples has been characterized to confirm the presence or absence of hemolytic anemia by evaluating the characteristic hematological features: Hemoglobin content (HGB), Hematocrit (HCT), Red Blood Cells (RBC), Mean Corpuscular Volume (MCV), Mean Corpuscular Hemoglobin (MHC) and Red-cell Distribution Width (RDW).

The preliminary outcomes are promising and allows to consider coupled TGA/Chemometrics an alternative, cheap and fast diagnostic method for a early detection of Sickle Celle Anemia.

Referecens

1. S. Azar, T. E. Wong. Sickle Cell Disease. A Brief Update. Medical Clinics of North America, 2016; 101: 375-393.
2. J.B. Schnog, A.J. Duits, F.A.J. Muskiet, H. ten Cate, R.A. Rojer, D.P.M. Brandjes. Sickle cell disease; a general overview. The Journal of Medicine, 2004; 62: 364-371.
3. R. Risoluti, S. Materazzi, F. Sorrentino, L. Maffei, P. Caprari. Thermogravimetric analysis coupled with chemometrics as a powerful predictive tool for ß-thalassemia screening. Talanta, 2016; 159: 425–432.

In-depth Proteomic Study of Plasma Proteins During Sport Activity

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In recent years, more and more people have joined the world of running and this increase is even more pronounced for marathon and half marathon. Physical activity improves overall health and counteracts metabolic pathologies. It is also well-known that exhaustive exercise is associated with free radical (FR) production and consumes the available antioxidants, especially during periods of intensive training. Depending on the nature, degree and duration of the physical activity, the different cell types of the body suffer varying levels of oxidative stress, which may threaten the athlete's well-being. The purpose of our study was to investigate plasma protein profiles of athletes before and after a half marathon. The immunodepletion of abundant proteins followed by untargeted mass spectrometry analysis allowed us to compare pre- and post-exercise blood samples in order to provide both qualitative and quantitative information. Interestingly, proteomic data showed the activation of both inflammatory response and detoxification process. In addition, the involvement of pathways associated to immune response, lipid transport and coagulation, was elicited. In addition, for the first time we have analyzed the proteomic profile changes in runners after half-marathon activity in order to survey the related systemic adjustments.

Plasma Proteome Profiles of Stable CAD Patients Stratified According to Total Apo CIII levels

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Apolipoprotein C-III was recently acknowledged as a prognostic marker for cardiovascular risk. High levels of Apo-CIII strongly correlate with hypertriglyceridemia and are associated with atherosclerosis and coronary artery disease (CAD).
Aim of the present research was to study the plasma proteome profiles of stable CAD patients characterized by different levels of total Apo-CIII. Two subgroups of CAD patients with divergent concentrations (under and upper the median concentration of the population distribution=10 mg/dL) of total circulating Apo C-III were examined using a shotgun proteomic approach. Through the use of a micro-LC SWATH-MS analysis we were able to quantify 180 plasma proteins: the data were then analyzed by bioinformatic tools and multivariate statistics. The fold change analysis and the Partial Least Square Discriminant Analysis showed a clear separation of the two groups. The dynamic processes that involve Apo C-III concentration in blood and its relation with all other plasma proteins were considered. The concentrations of Apo C-III, Apo E, retinol-binding protein 4 and alpha 1-antitrypsin were also validated using ELISA assays.
In this pilot study, the different expression of plasma proteins through the entire range of concentrations of Apo C-III was defined, suggesting possible new players involved in the APO C-III-associated process of arterial damage.

Cholesterol Content of Two Eggs a Day in Human Supply Noes Not Harm the Health of Healthy Individuals

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Chicken eggs are highly favored foods for their nutritional and functional properties due to the high content of proteins, lipids and micro nutrients e.g. vitamins and minerals. In the past years has been reported that the cholesterol contained in the egg yolk was an high contribution to the cholesterol recommended daily intake and consequently the nutritionists recommended a minor weekly consumption of eggs. In this study, the quantitative determination of cholesterol in chicken egg yolk was investigated. There are some conflicting views and results in relation to the analytical methods used for the cholesterol determination. An efficient, fast and reproducible method for cholesterol determination is then vital for the control of cholesterol uptake. This paper proposes a simple method for the rapid quantification of cholesterol in chicken eggs yolk by gas chromatography that could be used as a routine method for the rapid and sensitive determination of cholesterol.

Cholesterol content in a sample of 100 eggs purchased on the local market, ranging in 55-80 g interval of weight was analyzed. The results indicate that the cholesterol content is in the range of 140 - 210 mg (average value 175 mg/egg) instead of 250 mg/egg as reported in the literature. The difference of cholesterol content before and after transesterification, indicates that the cholesterol content as sterylester in the egg fatty part is negligible. The analytical procedure used, based on gas chromatography (Figure 1), allowed us to quantify the non polar fraction of the egg yolk fat, which is about the 75% of the total yolk fat weight, while the cholesterol content of the yolk is not related to the weight of the yolk itself and to the weight of the entire fatty part. The obtained results do not agree with the previously reported data allowing us to conclude that the cholesterol content in poultry eggs has been overestimated.

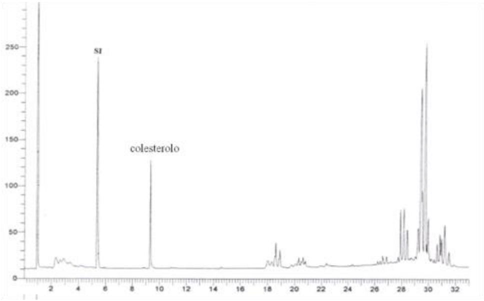

FIGURE 1. Gas chromatogram of free non polar lipid fraction of egg's fat. Cholesterol peak is separated from triglycerides and analyzed by means of internal standard (squalene). Column 65% phenyl methylslicone HT (TG), RTX 65-TG (Restek, Bellefonte, CA, USA); l=30 m; i.d.=0,25 mm; f.t. 0,25 µ.

Reference
1. Naviglio, D., Gallo, M., Grottaglie L.L, Scala, C., Ferrara L., Santini, A. Determination of cholesterol in Italian chicken eggs. Food Chemistry, 2012. 132(2): p.701-708.

LC-ES-MS/MS-Assisted Bile Acids Speciation In Biological Tissues In Permeability Studies Using Franz Cell Model.

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The intestinal adsorption of natural and new semisynthetic bile acid (BA) play a major role in their organ biodistribution and biological activity. BA as detergent-like compounds self-aggregate to form micelles with phospholipids and cholesterol. The critical micellar concentration and the micellar stability constant, pH, ionic strength plays a major role in the equilibrium between BA monomers and micelles and the related partition and diffusion across biological membranes. The monomer passive diffusion is related to its lipophilicity as evaluated by the octanol-water partition coefficient LogP. BA with different physicochemical properties including cholic, chenodeoxycholic, deoxycholic and 6-ethyl chenodeoxycholic acids have been studied for their permeability in biological tissues. It is generally considered that the BA physico-chemical characteristics are the most important factors contributing to their partition, permeation and diffusion. BA, if able to across membranes (LogP>1), diffuse in the layered tissue compartments and their permeability coefficient (Kp) calculated according to Fick's first law of diffusion, based on the steady state flux allow to evaluate the passive process efficiency. Moreover, additional thermodynamic interactions with binding proteins and specific receptor are involved in the net permeation process and therefore BA could be present in the biological fluids and compartment in different species, such as neutral/ionized monomer, simple BA micelles, mixed micelles, monomer-protein complex, monomer-receptor complex, all of these equilibrium species modulated by the pH and ionic strength. In order to define the species involved, an integrated analytical approach has been developed. BA were identified and quantified in the different biological fluids such as bile, simulated duodenum content, tissue sub-fraction by HPLC-ES-MS/MS as previously reported[1]. The method fulfils all the standard criteria and the limits of quantification (LOQ), were < 20 nM for each analyte. Surface tension experiment were performed using maximum bubble pressure method allowing to define the monomer-micelles equilibrium and the CMC. The LogP was measured as a function of the pH, ionic strength and BA concentration. Data of protein binding and specific receptor such as TGR5 (membrane) and FXR (cellular) thermodynamic affinity constants will be used to define the complex multiple equilibria present in the intestinal content/ tissue stirred and unstirred interface. The Franz diffusion tissue system using vertical cell has been used to measure the BA permeability as a function of the pH, initial concentration and ionic strength. The steady state flux (J, $\mu g\ cm^{-2}\ h^{-1}$) and lag time can be estimated. Data show that a BA with a high LogP such as DCA, despite an efficient partition in the tissue, present a delayed clearance from the tissue due to a strong interaction with the lipid domain of the tissue and additional interaction with FXR receptor. An intermediate LogP such as that of CA allows a more efficient and fast process. Modeling, understanding and characterizing the permeation process of BA with different structure and physicochemical properties through various biological membrane barriers and tissue is essential in order to predict the *in vivo* behavior and to explain their mechanism.

Reference
1. Roda Aldo, et *al.*; *Journal of Pharmacology and Experimental Therapeutics*, 2014, 350.1, 56-68.

The Combined Use Of Alkyl Chloroformate And Solid-Phase Microextraction For A Fast And Easy Assay Of Polyamines In Human Urine By Gas Chromatography-Triple Quadrupole Mass Spectrometry

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One of the decisive aspects to fighting cancer in an effective manner is early diagnosis and rapid treatment of this disease. In this respect, the development of new, rapid and cheap tumor diagnostic techniques represents one of the main targets of recent clinical research. Several studies have been focusing on the discovery of cancer biomarkers because their identification can be of crucial importance in early detection programs. Indeed, a high concentration of these molecules or in some cases just their detection can provide information on tumor occurrence, type of cancer, and disease progression at very early stages[1].

Polyamines are aliphatic amines with low molecular weight, which are essential for normal growth and cellular differentiation[2]. The marked increase of the biosynthesis of polyamines has been associated with rapid tumor growth, resulting in the increase of their level in urine and plasma[3]. Due to these findings, it is widely recognized that the polyamines are among the most important cancer biomarkers for early diagnosis and treatment.

The goal of this work is the development of a rapid and simple method for the quantification of free polyamines (i.e., putrescine, cadaverine, spermidine, spermine) and N-monoacetylated polyamines (i.e., N^1-Acetylspermidine, N^8-Acetylspermidine and N^1-Acetylspermine) in human urine. A preliminary derivatization with propyl chloroformate combined with the use of solid phase microextraction (SPME) allowed for an easy and automatable protocol involving minimal sample handling and no consumption of organic solvents. The affinity of the analytes toward five commercial SPME coatings was evaluated in univariate mode and the best result in terms of analyte extraction was achieved using the divinylbenzene/carboxen/polydimethylsiloxane fiber. The variables affecting the performance of SPME analysis were optimized by the multivariate approach of "Experimental design" and, in particular, a central composite design (CCD) was chosen. Analyses were carried out by gas chromatography-triple quadrupole mass spectrometry (GC-QqQ-MS) in selected reaction monitoring (SRM) acquisition mode. The developed method was validated according to the guidelines issued by the Food and Drug Administration (FDA). The satisfactory performances reached in terms of linearity, sensitivity, matrix effect, accuracy and precision make the proposed protocol suitable to be adopted for quantification of these important biomarkers in urine samples.

References

1. P.R. Srinivas, B.S. Kramer, S. Srivastava; "Trends in biomarker research for cancer detection"; *Lancet Oncol.*, 2001, *2*, 698-704.
2. A.E. Pegg; "Polyamine metabolism and its importance in neoplastic growth and a target for chemotherapy"; *Cancer Res.*, 1988, *48*, 759-774.
3. S.H. Lee, S.O. Kim, H. Lee, B.C. Chung; "Estrogens and polyamines in breast cancer: their profiles and values in disease staging"; *Cancer Lett.*, 1998, *133*, 47-56.

A Workflow For ESI-MS High Resolution Lipidomics Data Processing

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Lipids comprise a diverse group of biomolecules organized in height major categories with a considerable range of structural attributes and chemical properties. Great attention has been recently devoted to those compounds since it has been observed that variations in lipid profile may be related to several human diseases. Typically, individual species are identified and quantified with mass spectrometry (MS)-based platforms using sample preparation protocols and synthetic lipid standards if a targeted approach is followed. Alternatively, lipids can also be profiled with untargeted analysis, in which no synthetic lipid standards are used for quantification and lipid abundance is inferred from the arbitrary intensity values usually normalized to each class. In the latter case, the analysis of lipidomics data requires automation with the support of dedicated software. In the last years, several efforts have been shaped with the aim to analyze data from either shotgun experiments such as LipidView[1], LipidXplorer[2], ALEX[3]] or from liquid chromatography (LC)-MS such as LipidSearch[4] and LIMSA[5]. Note however that the only matching of *m/z* values without further data processing and validation can represent a major source of error. Thus, a first data deconvolution is necessary by using algorithms which allow for correct identification and correct isotopic overlap. Of course, a validation of results through the visualization of input data and obtained results is always required. By managing big lipidomics data sets, every proposed and above mentioned package exhibits some advantages and limitations. For instance, ALEX lipid database currently covers about 20,000 species divided in more than 85 lipid classes. Each lipid species in the database is annotated using the chemical formula, the mono-isotopic mass in both the positive and negative ionization mode, the lipid group, the lipid class and other information. More, ALEX database is also available as Microsoft Excel file to help enumerate and calculate formula and chemical mass for each species, so that the user can easily add a lipid class. On the other hand, it does not allow to correct for isotopic overlap, it is specific for high resolution MS and it is quite difficult to manage. By using LIMSA Excel add-in it is possible to find and integrate peaks in a mass spectrum for comparison with an internal list. This tool is also capable of correcting the overlap of isotopic patterns and quantify the lipid species identified by using internal standards. LIMSA has a friendly user interface and can be applied to any type of MS spectrum. LIMSA internal database cab be implemented by adding new lipid classes. A disadvantage of LIMSA is related to the assignment of some lipid species which are based only on *m/z* feature matching, providing an extensive list of "misleading" and improbable identifications. Conversely, ALEX database proposes more appropriate lipid assignments considering fatty acids really occurring in nature. The idea of this work is to integrate ALEX into LIMSA database with the aim to join the advantages of each software creating a new easy lipidomic platform. To do this, ALEX database has been downloaded and used as starting point for building a new written database that can be implemented into LIMSA. Finally, the whole developed workflow is applied to the lipidome analysis of a complex real sample of human plasma.

References
1. *C.S. Ejsing et al. Anal. Chem. 78 (2006) 6202–6214.*
2. *Shevchenko et al. PLoS ONE 7 (2012), e29851.*
3. *P. Husen et al. PLoS One 8 (2013), e79736.*
4. *R. Taguchi et al. J. Chromatogr. A 1217 (2010) 4229–4239.*
5. P. *Haimi et al. Anal Chem 78 (2006), 8324-8331.*

Emerging Contaminants In Food: Analysis Of Chocolate By UHPLC Coupled To High-Resolution Mass Spectrometry

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One of the great challenges in food safety is to assess the risks associated with the presence of emerging contaminants, chemical substances not mentioned in the Regulation but representing a potentially risk to human health. Emerging contaminants in food are increasing as a consequence of new industrial processes, agricultural practices, environmental pollution. Foods can be contaminated during the entire life of a product, from the collection of raw materials, during the whole production chain, to storage and consumption. Possible contamination sources are represented by parts of industrial plant or plastic objects in contact with the product also during meal preparation[1]. Since contamination may imply a risk to health, and has a negative impact on food quality, the European Union has taken measures to minimize their occurrence in foodstuffs. Therefore, an important trend of analytical chemistry is to develop fast and efficient procedures for the trace analysis of target and non-target compounds in food. Many researchers centered their attention on the analysis of simulants, while only few papers report results based on real food samples. This work was focused on chocolates and pralines production: industrial and hand-made processing of chocolates involves a contact of the product with plastic material. Previous studies on simulants under similar conditions of time and temperature reported migration of plastic additives[2], products of polymer degradation, colouring agents and non-intentionally added substances (NIAS)[3]. An important point regards the discover of oligomers of bisphenol A that could derive by unreacted species or polymer degradation. Their occurrence should be considered of high concern since they could be hydrolyzed *in-vivo* generating several bisphenol A units. Experiments were performed on three different chocolate types (dark, white and milk chocolate) and two simulant solutions (isooctane and ethanol) placed in contact with plastic objects of different shape and color. Migration tests were carried out in a climatic chamber and repeated three times according to the procedure described in legislation[4]. Since the degree of damage of the plastic surface is an important parameter affecting the migration, samples of different age, and submitted to different washing cycles, were examined. Analyses were performed by UHPLC-HRMS nano-system operating in capillary-flow mode coupled to a Q-Exactive mass spectrometer. Data dependent acquisition mode for targeted and untargeted analysis was exploited[5]. Results showed that old and new objects released different compounds. Kinetic curves were built by analysis of samples put in contact with polymeric materials for different time periods. Besides, a slight difference in the amount of oligomers released was found depending on the chocolate type. The possible correlation between age, degree of damage, and compound migration was explored.

References
1. J. Campo, Y. Pico, Emerging contaminants, in: Y. Pico (Ed.), Advanced mass spectrometry for food safety and quality, Comprehensive Analytical Chemistry, vol. 68, Elsevier, 2015, pp. 515-569.
2. C. Bignardi, A. Cavazza, C. Laganà, P. Salvadeo, C. Corradini, (2015) *Anal Bioanal Chem*, 407, 7917-7924.
3. C. Bignardi, A. Cavazza, C. Laganà, P. Salvadeo, C. Corradini (2017) *Food Control*, 71, 329-335.
4. European Commission (2011) Regulation (EC) No. 10/2011. *Official Journal of European Union, L 12*, 1-89.
5. C. Bignardi, A. Cavazza, C. Corradini, P. Salvadeo (2014) *J. Chromatogr. A*, 1372, 133-144.

A Simple And Rapid GC-MS/MS Method For The Determination Of Phytoestrogens In Soy Drinks

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Phytoestrogens are a family of nonsteroidal natural compounds, with the function of secondary metabolites in many plants, such as soy, legumes, alfalfa and hop. They are considered endocrine disruptors chemicals, since they can interact with the human endocrine system, through a range of mechanisms which have not been completely elucidated so far[1]. Because of these complicated mechanisms of action, the effect of phytoestrogens on humans can be detrimental or beneficial, depending on numerous factors, such as age, habits, exposure to other chemicals. In the recent years, many vegetal food, based on soy and legumes, are spreading in the market and this could cause an excessive consumption of phytoestrogens. For this reason, it is important to determine the concentration of phytoestrogens in this kind of matrices, to estimate the intake of these substances.

In our lab, we are developing and testing different chromatographic techniques, coupled to mass spectrometry, for the analysis of phytoestrogens in food, especially soy based products. HPLC-MS is usually preferred for the analysis of phytoestrogens[2], since the GC analysis requires a derivatization step[3]. Nevertheless, GC-MS is a much more affordable technique and so we developed a method for the determination of five common phytoestrogens, biochanin A, daidzein, genistein, formononetin and coumestrol.

The derivatization procedure was deeply studied, testing different derivatizing reagents and performing an experimental design to find the optimal conditions of the derivatization reaction with *N*,*O*-bis-(trimethylsilyl) trifluoroacetamide (BSTFA). The results showed that a derivatization of the analytes in the injection port was possible, making the analysis more rapid and simple. On the other hand, various instrumental parameters, related to the tandem MS detection, were optimized to enhance sensitivity and specificity of the analysis.

The final method consisted of the addition of the derivatizing reagent and immediate analysis by GC-MS/MS, with injection performed with a programmed temperature vaporizer (PTV). Low detection limits (0.1-17 µg L^{-1}) and high specificity were obtained for all phytoestrogens; calibration curves were built in the range of 8-500 µg L^{-1} and good precision (relative standard deviations of 4.7-6.1%) was reached for formononetin, daidzein and coumestrol. Some problems arose with biochanin A and genistein, whose derivatives exhibited low stability; consequently, the determination of these two phytoestrogens was characterized by low repeatability. The optimized method was tested on soy drink samples from a local drugstore: a simple solid phase extraction was performed on soy milks and the extracts were derivatized and analyzed. High concentration (4-16 mg L^{-1}) of daidzein and genistein were found, while the other phytoestrogens were in the range of 20-400 µg L^{-1}.

References
1. C.R. Cederroth, C. Zimmermann, S. Nef, Soy, Mol. Cell. Endocrinol., 2012, 355, 192–200
2. G.G.C. Kuhnle, C. Dell'Aquila, Y. Low, M. Kussmaul, S.A. Bingham, Anal. Chem., 2007, 79, 9234–9239
3. I. Ferrer, L.B. Barber, E.M. Thurman, J. Chromatogr. A., 2009, 1216, 6024–6032

Milk Authenticity By Ion-Trap Proteomics Following Multi-Enzyme Digestion

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The practice of adding adulterating substances (water, starch, sodium citrate, urea, sucrose, melamine, etc) in milk products in order to raise profits is worldwide employed. In addition, higher priced milk, coming from minor dairy species, such as goat and buffalo showing high nutritional and economical value, is often illegally integrated with the lower priced cow milk. The presence of species-specific proteins, different from those declared in label, may be a serious problem for people with allergies. The development of proper analytical methods is therefore essential to protect consumer benefits and product authenticity, as well as to detect economic frauds.

Several analytical techniques, including capillary electrophoresis[1], polymerase chain reaction[2], enzyme-linked immunosorbent assays[3] and two-dimensional gel electrophoresis (2-DE)[4], have been used to evaluate the content of mixtures of milk of different species

In this study, a proteomic approach for the detection of adulteration processes of specific milks in mixtures is proposed. Milk samples digested by trypsin and chymotrypsin have been analyzed by nanoLC-ESI-IT-MS/MS. A post-database processing was performed to obtain the sequence assignments[5]. In the complex overview of the strategies reported for the evaluation of milk authenticity, our approach is characterized by reduced instrumental costs and analysis speed. Indeed, the proposed method is quite rapid, with the only exception of the digestion step that, however, is usually performed overnight, and then does not represent a real extra-time of analysis. Moreover for the protein characterization few microliters of sample are required and directly analyzed by a single shot-gun analysis, without a previous separation. In addition to a direct evaluation of milk traceability at low level of adulteration, this method has confirmed the identification of two effective signature peptides related to bovine milk source (LSFNPTQLEEQCHI and HQGLPQEVLNENLLR from β-lactoglobulin and αS1 casein, respectively) allowing the detection of hidden allergens at adulteration levels down to 1%.

References

1. J.M. Herrero-Martínez, E.F. Simó-Alfonso, G. Ramis-Ramos, C. Gelfi, P.G. Righetti. Electrophoresis 21(2000) 633–640.
2. J.S. Guerreiro, P. Fernandes, R.G. Bardsley. International Dairy Journal 25(2012) 42–45.
3. I.P. Hurley, H. Elyse Ireland, R.C. Coleman, J.H.H. Williams. International Journal of Food Science and Technology 39 (2004) 873–878.
4. K. Hinz, P.M. O'Connor, T. Huppertz, R.P. Ross, A.L. Kelly. Journal of Dairy Research 79 (2012) 185–191.
5. D. Nardiello, A. Natale, C. Palermo, M. Quinto, D. Centonze. Talanta 164 (2017) 684–692.

Analytical Pyrolysis With In-Situ Derivatization, Py(HMDS)-GC/MS Of Condensed And Hydrolysable Tannins: A Flexible Characterization Technique

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Tannins are natural oligomeric phenols. They are fundamental materials for the food and leather industries, and are widely studied for their biological activity. Tannins can be extracted from several types of lignocellulosic biomasses, and so their study is also of great relevance in the field of biomass conversion.

The main challenge in the analysis and characterization of tannins is their wide compositional variety. Wet chemistry methods such as colorimetric assays can only provide information on the total content, with little to no means of speciation. Liquid chromatography techniques (TLC, HPLC) have been used to characterize both hydrolysable and condensed tannins, but provide poor results in terms of peak shape and resolution[1]. The use of analytical pyrolysis techniques in the study of tannins is less well documented[2], but such techniques seem to be promising in this field. Both solid and liquid samples can be analysed without pre-treatment steps, and speciation could be possible by the analysis of their pyrolysis products. In the present work, Py-GC/MS was used to identify the main pyrolysis products of both hydrolysable and condensed tannins, starting from the analysis of their building blocks (gallic acid, ellagic acid, catechin). Moreover, the use of in-situ derivatization using hexamethyldisilazane (HMDS) as derivatizing agent allowed us to improve the quality of the results in terms of peak shape and resolution. Thermal degradation mechanisms were also investigated by performing experiments at different pyrolysis times. The results were used to characterize natural tannin extracts. This work shows the first results and the potential of a widely applicable technique for the analysis of vegetable tannins.

References:
1. A. Romani et *al.*; *Journal of Pharmaceutical and Biomedical Analysis*, 2006, *41*, 415-420.
2. P. A. Case et *al.*; *Journal of Analytical and Applied Pyrolysis*, 2014, *107*, 250-255.

A New Method for The Determination Of Crocins As Markers Of Quality And Authenticity By UHPLC-MS/MS

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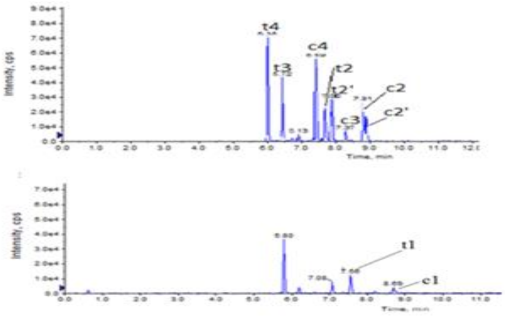
Saffron is a precious spice known as "red gold" obtained from the dried stigmas of the *Crocus Sativus* L. a plant of the Iridaceae family. Its importance is related to the peculiar quality and sensory properties, in particular aroma, colour and taste that are mainly due to the presence of safranal, crocins and picrocrocin, respectively.

Crocins are water soluble-carotenoids of saffron and they are glycosyl esters of crocetin with different sugar moieties, such as glucose, gentiobiose, neapolitanose or triglucose; they can be present in saffron in cis- and trans- isomeric forms[1]. They are known to exert various pharmacological effects on various illnessand anti-tumor effects by inhibition of cell growth[2]. When saffron is exposed to white fluorescent light, trans isomers change into cis ones[3].

The aim of this study is to determine the content of crocins isomers of saffron of different origin and obtained by different process conditions and to use the cis-trans content ratio as index of quality and authenticity.

Analysis was carried out by UHPLC-MS/MS. A preliminary step of the study implied the optimization of the extraction efficiency for both crocins. An experimental design plan was set including independent variables: extraction solvents (MeOH, H_2O, MeOH/ H_20 with different ratio), time and temperature of Ultrasound Assisted Extraction (USAE).

The best conditions found were: saffron powder (5 mg) were extracted with 1.25 mL MeOH/H_2O (50:50, v/v) for 15 minutes in ultrasonic bath at T=25°C (Fig.1).



Extracted ion currents (XIC) of the selected transitions obtained from the analysis of a saffron extract

Results have been processed by Principal Component Analysis (PCA). This study is confirming the feasibility to study crocins isomers as marker of quality and authenticity of saffron samples.

References
1. Lech K., Witowska-Jaroszb J., Jarosz M.; *J. Mass Spectrom*, 2009, *44*(12), 1661-7.
2. Aung H.H., Wang C.Z., Ni M., Fishbein A., Mehendale S.R., Xie J.T., Shoyama C.Y., Yuan C.S.; *Exp. Oncol.*, 2007, *29*(3),175-80.
3. Sarfarazi M., Jafari S.M., Rajabzadeh G.; *Food Anal. Methods*, 2015, *16*, 1–13.

Panoramic Overview on the Enantioselection Performance of Inherently Chiral Surfaces: a Comparison between Systems with Different Atropisomeric Cores and Stereogenic Elements

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Enantiorecognition is a key issue in advanced analytical chemistry, particularly concerning the biological and pharmaceutical field. Enantiomeric molecules, being mirror-image structures, have identical physico-chemical scalar properties, but opposite pseudo-scalar ones. When interacting with a racemic probe, chiral molecules can recognize the enantiomers through diasteromeric interactions. Similarly, chiral electrodes are required for enantioselective electroanalysis, and the development of "intelligent" electrodes capable of discriminating enantiomers, in particular molecules of biological and pharmaceutical importance, remains as one of the major challenges in electroanalysis. We have recently proposed the first synthetic inherently chiral electrode surfaces able to neatly discriminate as separate peaks (in terms of potential values) the antipodes of model chiral probes, also drugs, both as enantiopure and racemate[1,2]. We have also verified the general validity of the inherently chiral concept, which does not depend from the chemical nature of the atropisomeric scaffold, testing chiral surfaces electrooligomerized from starting monomers with different molecular design (*i.e.* bithiophene, bibenzothiophene, biindole and paracyclophane cores) and different stereogenic elements (stereogenic axis *vs* helix *vs* plane). In order to fully elucidate the enantioselection capability of all of these heteroaromatic systems we propose a detailed comparison (an example in Figure) of our inherently chiral surfaces with different atropisomeric core *vs* thiahelicene-based films *vs* "two floor" paracyclophanic oligomers.

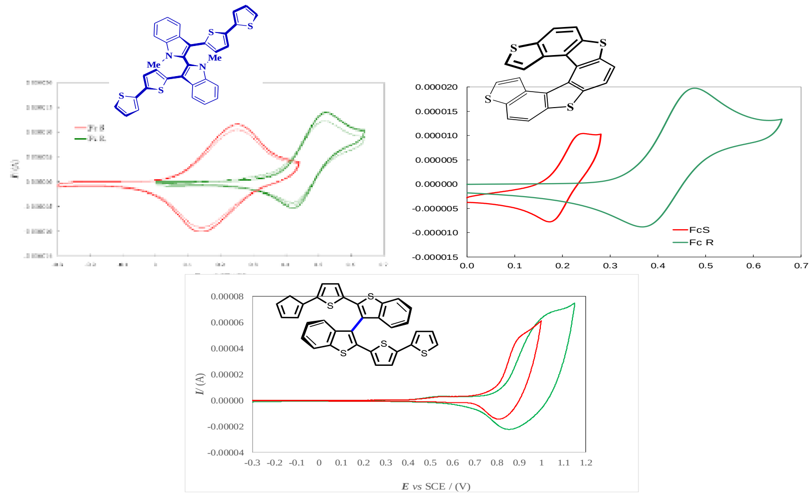

Figure. Enantioselection properties of inherently chiral oligomers with biindole, thiahelicene and bibenzothiophene units towards chiral ferrocenylic probes.

References
1. F. Sannicolò, S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P. R. Mussini, M. Panigati, M. Pierini, S. Rizzo, Angew Chem. Int. Ed., 53 (2014) 2623-2627.
2. S. Arnaboldi, T. Benincori, R. Cirilli, W. Kutner, M. Magni, P. R. Mussini, K. Noworyta, F. Sannicolò, Chem. Sci., 6 (2015) 1706-1711.

Direct Electrodeposition Of Gold Nanoporous (Aunps) Structure Onto Gold Electrode As Potential On-Line Biosensor Based On D-Fructose Dehydrogenase (FDH)

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In the last decades, nanomaterials have shown great advantages in terms of functional properties for a wide range of technological applications[1]. Metal nanoparticles provide a lot of advantages compared to macroelectrodes, such as enhancement of mass transport, catalysis, high effective surface area and control on the electrode conductive microenvironment. Gold nanoporous (AuNPs) can be synthesized by using a chemical approach and electrodeposition. The main advantages of the electrodeposition method are the thickness, roughness and size control of the AuNPs layer[2]. In this work AuNPs was directly electrodeposited onto a gold electrode (AuE) by using a two-steps method: 1) sweeping the potential in a 10 mM $HAuCl_4$ solution (supporting electrolyte 2.5 M NH_4Cl); 2) applying a potential -3 V vs. $Ag|AgCl_{sat}$[3,4]. Initially we optimized the different parameters that can affect the electrodeposition process, such as scan numbers, concentration of precursor solution, etc. Afterwards, the nanostructured electrodes morphology was studied by scanning electron microscopy (SEM). The so modified electrodes were characterized with $Fe(CN)_6^{3-/4-}$ by cyclic voltammetry and electrochemical impedance spectroscopy, and compared to the naked gold electrode (AuE) in order to determine the electroactive area (A_{EA}), electron transfer rate constant (k^0), real surface area (R_{SA}) and the roughness factor (ρ)[5]. The electrode was further modified by thiols with different aliphatic or aromatic structure, length and functional groups (e.g. -COOH, $-NH_2$, -OH) in order to provide a different charge onto the electrode, which may affect the orientation of *Gluconobacter japonicus* Fructose Dehydrogenase (FDH). D-Fructose dehydrogenase (FDH; EC 1.1.99.11) from *Gluconobacter japonicus* NCBR 3260 is a heterotrimeric membrane-bound enzyme complex with a molecular mass of ca. 140 kDa, consisting of subunits I (67 kDa), II (51 kDa), and III (20 kDa). Subunits I and II have a covalently bound flavin adenine dinucleotide (FAD) and three heme C moieties, respectively. FDH shows strict substrate-specificity to D-(-)-fructose and is utilized in diagnostic and food analyses. FDH provides large catalytic current density in DET bioelectrocatalysis. However, the electron transfer pathway is going from the sugar oxidation through the three heme C moieties, which exhibit different formal potential[6]. Finally, the electrode which showed the best results in terms of kinetic and analytical properties was tested for the detection of D-(-)-fructose in fruit juice samples as potential on-line biosensor for food industrial production processes[7].

References
1. S.D. Minteer, Top. Catal. 55 (2012) 1157-1161.
2. J. Zhang, M. Oyama, Anal. Chim. Acta 540 (2005) 299-306.
3. X. Dai, R.G. Compton, Anal. Sciences 22 (2006) 567-570.
4. G. Sanzó, I. Taurino, R. Antiochia, L. Gorton, G. Favero, F. Mazzei, G. De Micheli, S. Carrara, Bioelectrochemistry 112 (2016) 125-131.
5. I. Lavagnini, R. Antiochia and F. Magno, Electroanalysis 16 (2004) 505-506.
6. S. Kawai, M. Goda-Tsutsumi, T. Yakushi, K. Kano, K. Matsushita, Appl. Environ. Microb. 79 (2013) 1654-1660.
7. R. Antiochia, I. Lavagnini, F. Magno, Anal. Letters 37 (2004) 1657-1669.

Bioelectrochemical Characterization of ATG-Fructose Dehydrogenase (FDH_{atg}) from *Gluconobacter japonicus*: The Influence of Divalent Cations and Ionic Strength on Enzymatic Activity, Structure and Catalytic Current

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In the last decades, many redox enzymes and proteins have been investigated for the possibility of a direct electron transfer (DET) reaction between the active site of the enzyme and an electrode. DET reactions have received considerable attention for construction of biosensors and biofuel cells[1]. *Gluconobacter japonicas* fructose dehydrogenase (FDH) is a heterotrimeric-membrane-bound enzyme with DET characteristics. FDH catalyzes the oxidation of D-fructose to 5-keto-D-fructose. Subunit I (67 kDa) and II (51 kDa) comprise the substrate active flavin adenine dinucleotide (FAD) and additionally three heme c moieties as redox prosthetic groups, whereas subunit III (20 kDa) contains no cofactor and is presumed to be related to the stability of FDH[2]. In this work, the effect of Ca^{2+} and Mg^{2+} as well as ionic strength on the catalytic current of FDH modified electrodes were investigated by flow injection amperometry by drop-casting FDH onto graphite electrodes. Additionally, the activity of FDH was spectrophotometrically assayed by using both mono- and di-electron acceptors (ferricyanide, cytochrome c, and 2,6-dichloroindophenol) in the absence and presence of Ca^{2+} and Mg^{2+} at different ionic strength values. As FDH is a membrane-bound enzyme, so far impossible to crystalize, circular dichroism spectra were carried out under the same experimental conditions in order to verify possible structural changes in the secondary structure of FDH[3], allowing further considerations on the mechanism of DET.

References
J.A. Cracknell, K.A. Vincent, F.A. Armstrong, Chem. Rev. 108 (2008), 2439-2461.
S. Kawai, T. Yakushi, K. Matsushita, Y. Kitazumi, O. Shirai, K. Kano, Electrochem. Commun. 38 (2014), 28-31.
C. Her, J.E. McCaffrey, D.D. Thomas, C.B. Karim, Biophys. J. 111 (2016), 2387-2394.

Thermodynamic Study Of The Interaction Of NTA-Phosphonate Derivatives With The Main Cationic Components (H^+, Na^+, Mg^{2+} And Ca^{2+}) Of Natural Fluids.

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Aminophosphonates represent an important class of biologically active compounds, infact they are structural analogues of the corresponding aminoacids. They are widely used as corrosion inhibitors and they are effective chelating agents that tightly bind metal ions, preventing them from forming insoluble precipitates. Despite these molecules are very important in the industrial fields, only few papers deals with information about their acid-base properties in aqueous solutions[1]. In this paper, three molecules were studied: a) N-phosphonomethyliminodiacetic acid (NTAP), b) N,N-Bis(phosphonomethyl)glycine (NTAP2) and c) Nitrilotris(methylenephosphonic acid) (NTAP3). NTAP is an important intermediate for the production of Glyphosate, whose production is very high, being the most produced reaching 90,000 tons/year. NTAP2 is a plant growth regulator, affects chloroplast membrane proteins and increases sucrose levels in sugarcane and to cause chlorosis in maize. NTAP3 is used as power plants and for the prevention of the formation of calcium carbonate scale. Therefore, we focused our attention on the determination of the protonation constants in three different ionic media as NaCl, $(CH_3)_4NCl$ and $(C_2H_5)_4NI$ using ISE-H^+ potentiometry. The measurements at different temperatures, namely T = 283.15, 298.15 and 318.15 K, were performed only in $NaCl_{(aq)}$. At infinite dilution and at 298.15 K, the refined values of the first protonation constants are: = 11.41±0.01, 12.39±0.02 and 13.27±0.03 for NTAP, NTAP2 and NTAP3, respectively. The enthalpy changes relative to the first protonation step at infinite diluition and at 298.15 K are: -15.7±0.3 kJ mol^{-1}, -20.5±0.4 kJ mol^{-1} and -33.5±0.2 kJ mol^{-1} (same order). The dependence of protonation constants on ionic strength was studied by means of a Debye-Hückel type equation and the SIT (Specific ion Interaction Theory) approach. Solubility measurements were carried out only for NTAP in the three ionic media at 298.15 K, in order to determine the total solubility and the solubility of the neutral species, as well as the Setschenow and activity coefficients. In addition, the formation constants between the ligands studied and Ca^{2+} and Mg^{2+} were determined at I = 0.15 mol dm^{-3} in NaCl at 298.15K.

Reference
1. De Stefano C., Foti, C., Giuffrè, O. and Milea D. Complexation of Hg^{2+}, CH_3Hg^+, Sn^{2+} and $(CH_3)_2Sn^{2+}$ with phosphonic NTA derivatives. ***New J. Chem.,*** 2016,***40,*** 1443-1453.

Securing And Ensuring Sustainable Use Of Red Grape By-Products: Recovery Of Polyphenols And Assessment Of Their Antioxidant And Antitumoral Activities With Highly Predictive Human Cell-Based Biosensors

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Recently, there has been great social and environmental interest for the efficient reuse of agricultural industry residues. In fact, agriculture and food processing industry generate a huge amount of waste streams, as well as co- and by-products, that are often not properly taken care of, both in environmental and economic terms. The present work aimed at the recovery and characterization of polyphenolic compounds extracted from red grape pomace (Vitis vinifera L.), a winemaking by-product. Polyphenolic compounds of dried red pomace were recovered by different extraction methods (ultrasonic-assisted extraction UAE, Naviglio®-assisted extraction NAV and supercritical fluids technique SFE). A significantly amount of anthocyanins, above all malvidin-3-O-glucoside, was recovered from dried red pomace with UAE and NAV extractions. The best extracts contained high amounts of anthocyanins were explored to determine antioxidant and anti-cancer activities. We developed an *in vitro* chemiluminescent bioassay to determine xanthine oxidase (XO) activity, one of the major sources of ROS in living endothelial cells. Intracellular XO activity was measured in 5×10^3 human endothelial cells in less than 20 min with a luminol/catalyst-based chemiluminescence assay with a limit of detection of 0.4 µU/mL. Moreover, the IC50 value of oxypurinol, the active metabolite of the standard inhibitor drug allopurinol was determined; oxypurinol addition (ranging from 5.0 to 0.5 µM) caused a linear decrease in XO activity, with an IC50 of 1.0 ± 0.5 µM[1]. The extracts derived from UAE and NAV were measured (ranging from 10 to 0.0 ug/ml), obtaining an IC50 of 0,86±0,07 µg/mL and 1,27±0,08 µg/mL, respectively. Then, we investigated the antitumoral properties of both extracts in two highly predictive human cell models, leukemia and breast cancer, using a spectrophotometric approach with a new tetrazolium salt (WST-8) in respect to a standard cell counting method. WST-8 is a highly soluble tetrazolium salt in water, reduced to yellow formazan by the activity of intracellular dehydrogenase. The amount of formazan generated in the cells is directly proportional to the number of living cells (λmax450 nm). After 72h of incubation, UAE and NAV extracts (ranging from 50 to 0,1 µg/mL) exhibited a GI50 (50% growth inhibition) in human breast cancer cells of 28.2 ± 1.2 µg/mL and 16.1 ± 0.9 µg/mL, respectively, while in leukemia cells 6.9 ± 0.1 µg/mL and 6.9 ± 0.1 µg/mL and 4.0 ± 0.2 µg/mL, respectively. The doxorubicin antineoplastic drug (ranging from 10 to 0,1 µM) was used as standard, showing a GI50 of 0.13 ± 0.07 µM in breast cancer cells and 0.76 ± 0.09 µM in leukemia cells. The results support the possibility of exploiting the extracts coming from grape processing by-products as ingredients for functional and innovative products in the nutraceutical, pharmaceutical or cosmetic fields.

Reference
1. Caliceti C et al. Anal Bioanal Chem. 2016;408(30):8755-8760.

Characterization and shelf-life evaluation of gluten-free biscuits enriched with Chestnut flour

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Manufacturing of gluten-free products is usually characterized by the need of optimizing specific technological processes aimed at obtaining properties to fulfill consumer expectations, since the raw material used often gives poor results in terms of taste, aroma, consistency and nutritional properties. For these reasons, lately, different alternative ingredients are being tested with the aim of improving the final result.

Chestnut flour is a promising ingredient in this field, containing high quality proteins with a very good content of essential amino acids (4-7%), fibers (4-10%), and low fat (2-4%). Besides, it also contains vitamins and microelements[1].

It has been successfully used in few cases for bread and pasta production. Nevertheless, few data are at present available regarding the technological characterization and the shelf-life of chestnut based products[2].

This work was aimed at the optimization of a recipe for the production of gluten-free biscuits. Different samples were prepared by mixing chestnut flour and gluten-free flour in different proportions. Obtained products were evaluated by analysis of chemical-physical properties, colorimetric measures and sensory analysis. The behavior of the biscuits during 60 days of shelf-life has also been monitored.

Since oxidative stability is an important parameter affecting food shelf-life, the product was submitted to analysis by Oxitest (VELP Scientifica, Italy), a reactor based on the use of high temperature and over-pressure of oxygen allowing to easily measure a sample oxidative stability by accelerating the oxidation process.

Obtained data showed good and promising results since the increase of percentage of chestnut flour in the dough lead to a product with improved colour, harder texture, better taste and enhancement of oxidative stability, opening new perspectives in the use of chestnut flour for preparation of gluten-free products.

References

1. Chenlo, F., Moreira, R., Pereira, G., Silva, C.C., 2007. Evaluation of the rheological behaviour of chestnut (castanea sativa mill) flour pastes as function of water content and temperature. Electronic Journal of Environmental Agriculture and Food Chemistry 6 (2), 1794–1802.
2. Dall'Asta C., Cirlini M., Morini E., Rinaldi M., Ganino T., Chiavaro E., (2013). Effect of chestnut flour supplementation on physico-chemical properties and volatiles in bread making, LWT - Food Science and Technology 53-233-239.

Pseudo-ELISA Assay Based on Molecularly Imprinted Nanoparticles for the Determination of Hepcidin.

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Robust synthetic receptors able to recognize a target analyte of clinical relevance and prone to integration into sensing and assay platforms are an open challenge in the analytical panorama. In order to meet these requests, we exploited the technology of Molecularly Imprinted Polymer (MIP), i.e. a template-assisted synthesis in which monomers are polymerized in the presence of the analyte of interest, called template, to create cavities onto the growing polymer, which possess geometrical and chemical complementarity towards the template itself, in similarity to biological receptors[1,2]. Since MIPs exhibit stability to harsh conditions, low cost of production, ease of integration to electronics and tailor made selectivity, they could represent the alternative to antibody in immunoassays[2-5].

Here, we aimed at targeting Hepcidin, which is the main regulator of iron homeostasis[6] and has important clinical implications[7] but, given its tightly packed 3D-structure and its high conservation over the evolutionary ladder, its dosage proved to be not trivial for decades. Therefore, we exploited Hepcidin-addressed MIP nanoparticles (MIP-NPs)[8] to develop a pseudo-ELISA assay.

The MIP-NPs were synthesized to 20-60 nm in diameter; the functional characterization indicated the ability of MIP-NPs to selectively recognize Hepcidin with high affinity (low nM). The deposition of MIP-NPs onto the microplates and the protocol for Hepcidin measurement were considered and optimized step-by-step, achieving a range of response of 1-100 nM and LOD of 0.1 nM. Serum samples spiked with known Hepcidin concentrations (1, 10 nM) were used to evaluate the matrix effect on the response of the pseudo-ELISA.

In conclusion, our results highlighted both the MIP-NPs potential in terms of robustness, affinity and detection limits, and the limitations concerning the deposition protocol and the matrix effect, thus contributing to the MIP-based pseudo-ELISA development.

References
1. Wulff G. et al. Angew. Chem. Int. Ed. 1972, 11: 341.
2. Vlatkis G. et al. Nature 1993, 361:645-647;
3. Haupt K. et al. Anal. Chem. 1998, 70:628-631;
4. Chianella I. et al. Anal. Chem. 2013, 85:8462–8468;
5. Smolinska-Kempisty, K. et al. Sci. Rep. 2016, 6:art. no. 37638;
6. Piperno et al. J. World Gastroenterol. 2009, 15:538-551;
7. Ganz T. Physiol. Rev. 2013, 93, 1721-1741;
8. Cenci et al. J. Nanobiotechnol. 2015, 13:art. no. 51.

A New, Rapid Bioluminescent Yeast Reporter Gene Bioassay For Quantitative Estrogen-Like Endocrine Disruptors Bioavailability Detection.

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Living cells (bacteria, yeast and mammalian cell lines) have been widely exploited for biosensing as they provide useful information about the bioavailability of target analyte[1]. Nonetheless, one of the main drawback of cell-biosensors based on reporter gene technology is the long assay time (hours) due to the slow RNA production of the reporter enzyme upon induction and its accumulation to achieve the needed detectability. Here we report the development of a improved bioluminescent yeast-based whole-cell bioassay which provide a fast (15 min) and sensitive detection of estrogenic compounds in 96-well microplate format. In particular, *S. cerevisiae* cells were genetically engineered to express the human estrogen receptor α (hERα) and the Nanoluc luciferase in response to compounds able to activate the estrogen signalling pathway. Nanoluc luciferase was used as BL reporter since it represents the brightest luciferase available to date (150-fold brighter than firefly luciferase), emitting at 460 nm, using the coelenterazine analog furimazine as BL substrate. In addition, its small size (only 19KDa) and the absence of post-translational modifications and disulphide bonds, enable rapid synthesis and folding of the reporter thus reducing response time. The Nanoluc luciferase coding sequence was further optimized to increase its expression efficiency in yeast cells, and the use of a destabilized variant, allowed to reduce the background expression obtaining a rapid response upon induction by target analyte. The estrogen bioassay is performed in 96-well plates by incubating 90µL of yeast culture ($1,5x10^6$ cells/well) with 10µL of sample at room temperature (25°C) for 15 minutes, (compared with 2.5h of previously published yeast estrogen assays) making it the fastest BL yeast biosensor developed to date. Luminescence measurements are then performed with a luminometer without washing steps, by simple addition of 50µL of a custom BL substrate containing 10µM furimazine in a yeast-specific lysis buffer (Y-PER), optimized to provide a glow-type emission. The developed yeast bioreporter respond to 17-beta estradiol (selected as model analyte) with a limit of detection of 0.03nM and an EC50 of 1.5nM. The biosensor response to estrogenic compounds (e.g. diethylstilbestrol) and to several endocrine disruptors (i.e. bisphenol A, F and S) in spiked water samples is reported. In the perspective to apply the developed yeast bioreporters for actual on-field analysis, we also integrated yeast cells with a smartphone-controlled GoPro Hero5 camera as light sensor. To this end a 3D printed adaptor was fabricated to hold the GoPro camera and to house a custom 3D printed multi-well cartridge containing immobilized yeast bioreporters. This configuration combines the use of standardized sensitive detector with smartphone functionalities (i.e. connectivity, data elaboration, geo-tagging and the possibility to develop custom App), resulting in a versatile, user-friendly biosensing platform. Preliminary results obtained with the integrated device are presented.

Reference
1. Cevenini L, Calabretta MM, Lopreside A, Tarantino G, Tassoni A, Ferri M, Roda A, Michelini E. Anal Bioanal Chem. (2016) 408:8859-8868.

Synthesis And Analytical Characterization Of A Dual-Acting Pt(Iv) Prodrug With Potential Antitumor And Anti-Inflammatory Activities

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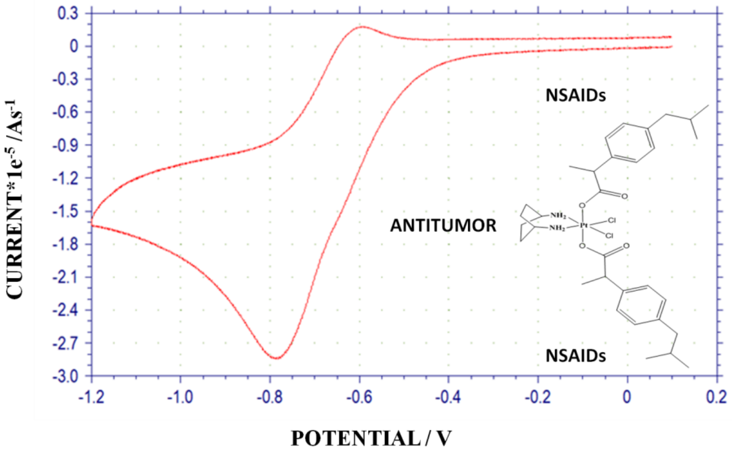
Pt(IV) complexes are organometallic antitumor prodrugs, activated *in vivo* to Pt(II) complexes with an irreversible reduction mechanism by endogenous biomolecules (glutathione, ascorbic acid)[1]. Reduction potential of those Pt(IV) complexes varies depending on axial ligand; specifically, it has been found that optimal values for in vivo reduction are obtained when platinum axial positions are functionalized with carboxylate groups[2]. In this work, the complex *cis*-*trans*-*cis*-[$PtCl_2$(*RS*-Ibuprofen-H)$_2$(*cis*-1,4-DACH)] was synthesized to obtain a potential prodrug having both antitumor and anti-inflammatory action. This can be achieved functionalizing both the axial positions of [$PtCl_2$(*cis*-1,4-DACH)] (kiteplatin) with two ibuprofen molecules. Ibuprofen was extracted from Brufen® commercial expired tablets, kiteplatin was synthesized as reported in the literature[3]. The synthesis *cis*-*trans*-*cis*-[$PtCl_2$(*RS*-Ibuprofen-H)$_2$(*cis*-1,4-DACH)] was carried out by adapting the procedure reported in (4,5). *Cis*-*trans*-*cis*-[$PtCl_2$(*RS*-Ibuprofen-H)$_2$(*cis*-1,4-DACH)] and its precursors were characterized by multinuclear NMR analysis and x-ray photoelectron spectroscopy (XPS) to determine Pt chemical oxidation state. The complex was electrochemically characterized by cyclic voltammetry to evaluate the possibility of reduction. in vivo. A reduction potential of -0.93V was found, whose value is compatible with *in vivo* reduction and consistent with analogous Pt(IV) complexes reported in literature (2). Perspective studies will be focused on the evaluation of *in vitro* cytotoxicity against human cancer cell lines.



References:
1. Hall M. D.et al., *Coordination Chemistry Reviews* 232.1 (2002): 49-67.
2. Choi S. et al., *Inorganic Chemistry* 37.10 (1998): 2500-2504.
3. Petruzzella E. et al., *Inorganic Chemistry* 52.5 (2013): 2393-2403.
4. Neumann W. et al., *ChemMedChem* 9.6 (2014): 1150-1153.
5. Neumann W. et al., *ChemMedChem* 10.1 (2015): 183-192.

Deposition of Palladium particles on glassy carbon surface modified by monolayer choline film and its electrochemical characterization

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The properties of palladium group metals have made them an invaluable source of active materials with a wide range of electrochemical applications and the definition of adequate deposition procedures of modulated-size nanoparticles is of key importance in many fundamental scientific and technological contexts[1,2]. Thus, deposition strategy of these active metals plays a fundamental role on the final properties of the prepared material. Choline is an essential nutrient for cell membrane function[3], but is also widely applied to metal and/or alloy electrodeposition procedures[4,5,6], where choline can be covalently grafted on glassy carbon surfaces using cyclic voltammetric methods (CV), forming stable cationic monolayer-modified electrode (GC/Ch). In particular, thick pure Pd particles were useful deposited from choline-palladium solutions without the addition of surfactant species and these resulting composite materials showed excellent properties on solderability and corrosion resistance[6]. In this study, a new electrodic material is based on the electrodeposition or adsorption of Pd ions on the GC/Ch electrode substrate. The choline film was electrodeposited on the GC surface by cycling the potentials between – 1.7 V and 1.8 V vs SCE; then Pd was electrodeposited by CV or directly adsorbed on the GC/Ch from acid solution containing K_2PdCl_6 1.5 mM. The effects of several experimental conditions such as: applied potentials, time of electrodeposition or adorption, choline concentration, etc. on the kinetics of Pd loading are considered and critically evaluated. The modified electrodes defined GC/Ch/Pd, were characterized by SEM and electrochemical techniques. The preliminary results confirm the presence of a globular and homogeneous dispersion of Pd particles on the GC/Ch substrate electrode with a considerable physical and chemical stability after prolonged electrochemical treatments. In addition, the study shows that the modified electrode GC/Ch/Pd exhibits a significant electrocatalytic activity toward oxidation of some compounds such as hydroxylamine, dopamine, epinephrine and common aminoacids in both acid and alkaline conditions.

References
1. C.R.R. Rao, D.C. Trivedi; Coord. Chem. Rev., 249 (2005) 613-631.
2. S. Guo, E. Wang; Nano Today 6, (2011) 240-264.
3. P.I. Holm, P.M. Ueland, G. Kvalheim; E.A. Lien, Clin. Chem., 49 (2003) 286-294.
4. J.Li, H. Xie, J. Appl. Electrochem., 42 (2012) 271-277.
5. P. Wang, Z. Mai, Z. Dai, Y. Li, X. Zou, Biosensors and Bioelectronics, 24 (2009) 3242-3247.
6. Y. Wang, W. Li, W. Wang, N. Mitsuzak, W. Bao, Z. Chen, Thin Solid Films, 586 (2015) 35-40.

PQQ-Dependent Glucose Dehydrogenase On Modified Carbon Nanotubes: Polythiophene Supported Electron Transfer For Sensing Applications

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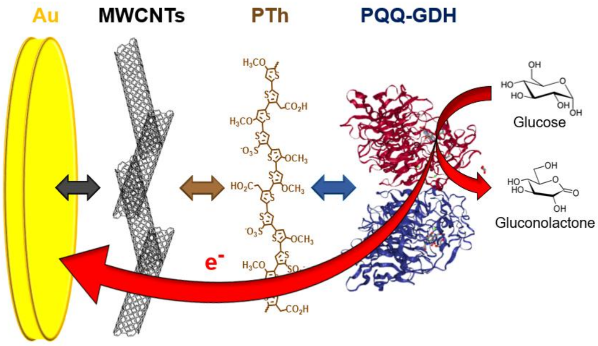
Conductive polymers are very attractive in the field of electrochemical biosensors. The intrinsic conductivity and the possibility to equip the chains with different functional groups by choosing the proper monomers make them very useful to improve the connection between the electrode and the redox center of an enzyme. In this context, polythiophene derivatives have only recently been employed in biosensing field in order to immobilize some enzymes like glucose oxidase, catalase or laccase. Anyway the use as conductive wiring matrix has not been fully exploited yet. Pyrroloquinoline quinone dependent glucose dehydrogenase (PQQ-GDH) has been extensively studied for biosensors and biofuel cells development thanks to its high catalytic activity and oxygen insensitivity. The redox active site is however embedded in the protein structure, so it is not easy to achieve an efficient direct electron transfer (DET). In this work, polythiophene copolymers (PTh) have been used as modifier for electrode surfaces in order to allow the immobilization of active PQQ-GDH and to simultaneously improve the direct electrical connection of the enzyme with the electrode. Polymer films were electrosynthesized onto carbon nanotubes (MWCNTs) modified gold electrodes from mixtures of 3-thiopheneacetic acid ($ThCH_2CO_2H$), 3-methoxythiophene ($ThOCH_3$) and, eventually, 2-thiophenesulfonic acid ($ThSO_3^-$) using a pulsed deposition method. Polythiophene deposition significantly improves the bioelectrocatalysis of PQQ-GDH. The process starts at -0.2 V vs. Ag/AgCl and allows glucose detection at 0 V vs. Ag/AgCl. Several parameters of the electro-polymerizing method were evaluated to maximize the anodic current output after enzyme coupling. Polymer deposition has been performed first in acetonitrile which required then a transfer into the aqueous system. However, electrosynthesis performed in an aqueous solution verified that also in this case successful electrode modification is feasible. Catalytic currents for the coupled PQQ-GDH have been found to be significantly higher. The electrode modifications were characterized by SEM, EDX, FTIR, XPS and UV-Vis. The obtained results suggest a further investigation of this kind of polymers and, in particular, the study of the interaction with other enzymes in order to employ them in building up biosensors and biofuel cells.



Amperometric Genosensor Based On PNA Probes Implemented On Carbon Nanotubes-Modified Screen Printed Electrodes

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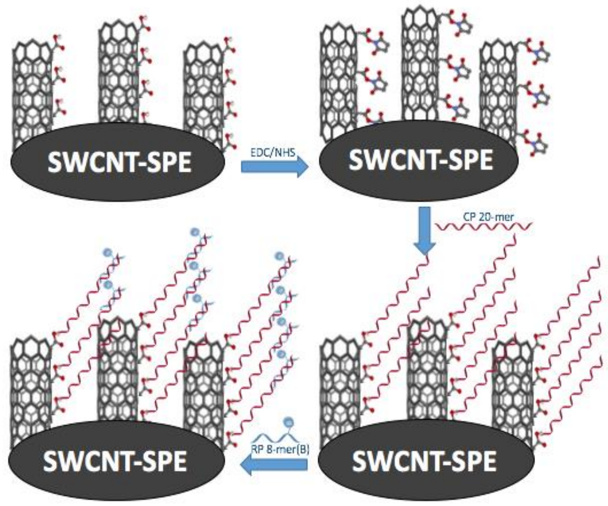
Nucleic acid-based biosensors (genosensors) have received great attention in the past decade, nucleic acids being promising molecular probes due to the ease of functional modification, the specificity for base pairing, and the predictability for intermolecular or intramolecular interactions. In a research program dealing with the development of innovative sensors as powerful analytical tools for assessing food safety[1,2], we combined performance of DNA-mimic probes based on Peptide Nucleic Acids (PNA) with the enhancing properties of carbon nanotubes (CNTs) as binding substrates on Carbon Screen Printed Electrodes (CSPEs). The findings of our previous studies[3], focused on the use of the same PNA probes on all-gold SPEs, evidenced best results using a non-competitive approach, based on the binding of a target DNA ascribable to "Roundup-Ready (RR)" transgenic soy by a PNA-Capture Probe (CP)-functionalized sensor, followed by the hybridization with a properly synthesized PNA-Reporter Probe (RP). The latter bears a biotin tag, capable of strong interactions with a streptavidin-alkaline phosphatase conjugate, which converts a substrate into an electroactive species. In this work, we experimented the use of CNT-modified electrodic platforms in order to reach higher loading capability of CP, if compared to gold substrates combined with Self-Assembled Monolayers from mercaptoundecanoic acid as linkers.



Another crucial aspect deals with the nature of the RP, since we noticed the formation of CP/Target-DNA/RP adduct when using PNAs both for capture and reporter probes. To overcome this limit, we moved to DNA-based RPs with the same oligonucleotidic sequence, obtaining encouraging results in terms of signal inhibition associated to hybridization of the target DNA up to nanomolar scale. Further studies currently ongoing are focused on the comparison of such inhibitive approach with the use of a sandwich-type assay based on the use of a longer DNA target, showing hetero-complementarity with CP and RP. Further improvements in terms of sensitivity enhancement could be also reached by conjugation of RPs with molecular nanomaterials such as dendrimers. The performance of polyamidoamine (PAMAM) dendrimers were already demonstrated in our previous studies concerning the development of competitive[4] and noncompetitive[5] immunosensors. These strategies will be further investigated to optimize the DNA assay protocols aimed at specific recognition of transgenic material at trace levels for GMO food labelling purposes.

References
1. A. Manfredi, M. Giannetto, M. Mattarozzi, M. Costantini, C. Mucchino, M. Careri; *Anal Bioanal Chem*, (2016) 7289–7298;
2. M. Giannetto, E. Umiltà, M. Careri; *Anal. Chim. Acta*, 806 (2014) 197–203.
3. S. Fortunati, MsSCI thesis, 2016.
4. M. Giannetto, E. Maiolini, E.N. Ferri, S. Girotti, G. Mori, M. Careri; *Anal. Bioanal. Chem.*, (2013) 737–743.
5. M. Giannetto, L. Mori, G. Mori, M. Careri; *A. Mangia, Sens. Act. B*, (2011) 185–192.

Selective Detection Of Halogenated Aromatic Hydrocarbons In Water With Piezoelectric Sensors Coated With Electropolymerized (2,2’bithiophene) Functionalized Cavitands

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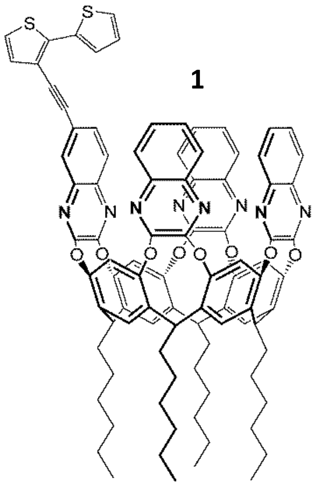

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New sensing coatings for piezoelectric sensors developed on gold-coated quartz crystals for Electrochemical Quartz Crystal Microbalance (EQCM) were electrosynthesized and characterized. The monomeric receptor **1** unit consists of cavitands functionalized at the upper rim with quinoxaline moieties, one of which bearing the bithiophene functionality connected *via* an unsaturated spacer arm. Previous studies carried out during the design of the monomeric unit evidenced as the use of 2,2’bitiophene building blocks is a crucial aspect for the reactivity of the receptors toward the electropolymerization, since the parent cavitand functionalized in the same position with a single thiophene unit was not capable to undergo electropolymerization, due to reduced reactivity of the monomer and steric hindrance of the system[1-3].

The cavitand functionalized with 2,2’bitiophene monomeric unit presented excellent performance in terms of reactivity, regularity of the polymer growth as well as compactness of the layer deposited on the gold surface of the crystals. The electropolymerization process, carried out under potentiodynamic conditions by cyclic voltammetry, was highly reproducible, as shown by the frequencymetric control of the growth (Figure 1). Analyte *host-guest* inclusion in cavitands was evaluated by insertion of the polymer-coated piezoelectric quartz in a 100-µL flow cell connected to a peristaltic pump. Continuous dynamic flow experiments carried out with aqueous solutions of different chlorinated aromatic and aliphatic hydrocarbons evidenced a remarkable selectivity for halogenated aromatic hydrocarbons, with frequency shifts increasing with the chlorination degree of the benzenes. A less intense but significant interaction was also observed with saturated and unsaturated chlorinated aliphatic hydrocarbons, whereas non-chlorinated aliphatic molecules did not give raise to significant frequency shifts.

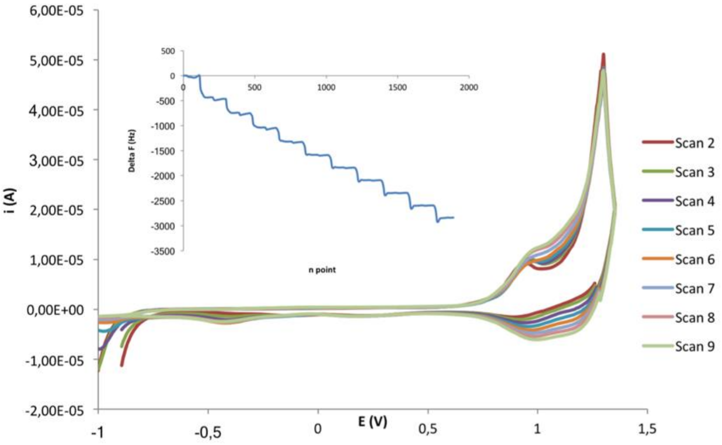

Figure 1: CV scans and frequencygrams (inset) recorded during the electropolymerization of the cavitand 1

References
1. M. Giannetto, G. Mori, A. Notti, S. Pappalardo, M.F. Parisi, Chem. Eur. J. 7 (2001) 3354-3362;
2. M. Giannetto, V. Mastria, G. Mori, A. Arduini, A. Secchi, Sens Act B 115 (2006) 62–68;
3. M. Mattarozzi, M. Giannetto, A. Secchi, F. Bianchi, J. Chromatogr. A, 1216 (2009) 3725–3730.

Innovative gold-free carbon nanotubes/chitosan-based competitive immunosensor for determination of HIV-related p24 capsid protein in serum

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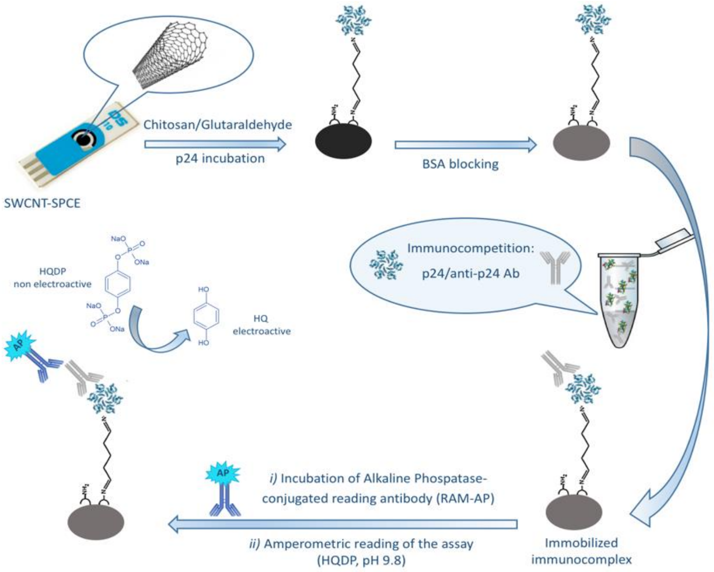
In the last decade, the need for simple, rapid, sensitive, specific, and inexpensive screening methods for diagnosis of HIV infection led to focus the attention on the HIV1-related capsid proteins p24 [1]. This protein is expressed in the core of the viral cell and occurs in blood-circulation since the first few weeks after infection, making it an useful biomarker for early diagnosis purposes. In this work we developed and validated the first competitive electrochemical immunosensor for the detection of HIV-capsid protein p24 as a simple, easy-to-use and promising tool for screening of sample for early diagnosis of HIV infection. The immunodevice was implemented on disposable gold-free Single-Walled Carbon Nanotubes-functionalized Screen-Printed Electrodes (SWCNT-SPEs) to take advantage of CNT properties in terms of enhancement of electrochemical active area, more efficient immobilization of bio-receptors and improvement of the electronic transfer process, aimed to a signal enhancement. The competitive sensor[2,3] is based on the immobilization of the target protein on the electrodic surface, through chitosan/glutaraldehyde system, as simple linker able to ensure in mild conditions a robust immobilization and a good exposition of the p24 for the interaction with the mouse anti- p24 IgG1. The immunosorbed antibodies were finally detected by an Alkaline Phosphatase-labelled Rabbit Anti-Mouse (RAM-AP) reading antibody. The immunosensor setup as well as the experimental conditions for the execution of the assay were optimized by means of a two-factor and three levels experimental design aimed to find the best concentration of the immunoreagents[4]. The competitive immunosensor exhibited good analytical performance in untreated human serum in terms of specificity, sensitivity and absence of matrix effect. No significant cross-reactivity from other serum markers, such as CA125 and CEA, was observed. The performance of the realized device, coupled with the advantages of an easy preparation, low-cost and portability of the instrumentation, makes it an analytically robust diagnostic tool valuable for implementation of large-scale screening programs for early diagnosis of seropositivity.



References
1. K. Teeparuksapun, M. Hedstrom, E.Y. Wong, S. Tang, I.K. Hewlett, B. Mattiasson; *Anal. Chem.*, 2010, *82*, 8406–8411.
2. M. Giannetto, E. Umiltà, M. Careri; *Anal. Chim. Acta*, 2014, *806*, 197–203.
3. M. Giannetto, E. Maiolini, E.N. Ferri, S. Girotti, G. Mori, M. Careri; *Anal. Bioanal. Chem.*, 2013, 737–743.
4. A. Manfredi, M. Giannetto, M. Mattarozzi, M. Costantini, C. Mucchino, M. Careri; *Anal Bioanal Chem*., 2016, 7289–7298.

Dynamic Spectro-Electrochemical Study of Pd in Fuel Cells with FEXRAV

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To fight the inexorable increasing of energy demand and pollution, it is crucial to develop highly efficient and clean energy conversion devices. In fact, current technologies have a bad impact on the environment or require great energy and raw material costs[1]. A winning approach is the controlled conversion of chemical energy to electricity from renewable sources[2]. For this reason, devices such as fuel cells are very interesting. In particular, ADAFCs (Alkaline Direct Alcohol Fuel Cell) are very promising because, in addition to producing high-power electrical energy and efficiency, they use cheaper catalysts than the commonly used platinum and are industrially attractive for the production of acetates.

These devices use a palladium-based catalyst, whose efficiency tends to decrease after hours of work. It is therefore essential to study the reaction mechanisms and behavior of the species on the electrode in order to increase the durability and preserve the efficiency of these devices. To achieve these results, it is important to understand how the Pd-based catalyst poisoning occurs to prevent it. Very important information is provided by the state of valence and structure of the catalytic material. Electrochemical and spectroscopic studies that are commonly conducted are unable to provide sufficiently accurate answers; for this reason, a relatively new technique has been used combining X-ray spectroscopy and dynamic electrochemistry: the FEXRAV (Fixed Energy X-ray Absorption Voltammetry)[3]. In our knowledge[3,4,5], this is the first documented use of FEXRAV on ADAFC to study the behavior of palladium and very interesting results have been achieved.

FEXRAV records variations in X-ray absorption and/or fluorescence intensity at a fixed energy, while the electrode potential varies. With the help of synchrotron light, it is possible to carefully follow the transition between the different valence states of the observed elements during the execution of classic electrochemical techniques: thus, FEXRAV results a very promising technique to study the evolution of electrocatalytic materials under operating conditions.

References
1. European Commission, Critical Raw Materials for the EU, (2010).
2. S.P.S. Badwal, S. Giddey, A. Kulkarni, J. Goel, v Basu. Applied Energy 145, 80–103, (2015)
3. A. Minguzzi, O. Lugaresi, C. Locatelli, S. Rondinini, et al., Anal. Chem. (2010), 85, 7009-7013.
4. A. Minguzzi, O. Lugaresi, E. Achilli, C. Locatelli, A. Vertova, et al., Chem.Sci. (2014), 5, 3591-3597.
5. S. Rondinini, O. Lugaresi, E. Achilli, C. Locatelli, et al., J. Electroanal. Chem. (2016), 766, 71–77.

Detection Of Organophosphorus Pesticides Using A DNA-Based Sensor

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In this work, we propose an electrochemical DNA-based sensor for sensitive multidetections of profenofos, an organophosphorus pesticide, based on a competitive format and disposable screen-printed arrays. To improve the sensitivity of the DNA-based sensor, polyaniline film and gold nanoparticles were progressively electrodeposited on the graphite screen-printed electrode surface by cyclic voltammetry[1,2]. Gold nanoparticles were then employed as platform for the immobilization of thiol-tethered DNA oligonucleotide sequence complementary to the DNA aptamer. Different profenofos solutions containing a fixed amount of biotinylated aptamer by DNA-based arrays were analyzed. Streptavidin-alkaline phosphatase conjugate was then added to trace the affinity reaction. The enzyme catalyzed the hydrolysis of 1-naphthyl phosphate to 1-naphthol. The enzymatic product was detected by differential pulse voltammetry. A decrease of the signal was obtained when the pesticide concentration was increased, making the sensor work as signal off sensor. Various experimental parameters of the realized DNA-based nanostructured sensor were studied and optimized using optical and electrochemical techniques. Under optimized conditions by testing key experimental parameters, a dose-response curve was constructed between 0.05-10.0 µM profenofos concentration range. The selectivity of the DNA-based sensor was also confirmed by the analysis of non-organophosphorus pesticides.

References
1. Rapini R., Cincinelli A., Marrazza G.; "Acetamiprid multidetection by disposable electrochemical DNA aptasensor"; *Talanta*, 2016, *161*,15-21.
2. Saberi R. S., Shahrokhian S., Marrazza G.; "Amplified electrochemical DNA sensor based on polyaniline film and gold nanoparticles"; *Electroanalysis*, 2013, 25,6,1373-1380.

Anchoring Of His-Tag-Rab7 Protein On Nanoporous Silicon. Toward Surface Imprinting For Optical Sensing Applications.

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Molecular imprinting is a universal concept to generate materials with "molecular memory" by performing a polymerization of suitable functional monomers in the presence of a target molecule acting as a template. The subsequent removal of the template creates recognition sites in the molecularly imprinted polymer (MIP) that can, further on, selectively rebind the target[1]. Although this concept proved to be successful in preparing selective sorbents for compounds of small molecular weight (~200–1200 Da), several specific problems can arise if the target is a macromolecular protein[2] as the classical imprinting methodologies fail to address the peculiarities of protein targets. The difficulties are largely attributed to the intrinsic properties of the proteins. Due to their fragility irreversible conformational changes may occur during polymerization; moreover, the large size of the proteins makes them difficult to remove from, or rebind to a highly cross-linked polymeric network. Among the approaches introduced during the past decade to overcome the barriers of protein imprinting[2], surface imprinting emerged as the main strategy for macromolecular imprinting. This approach restricts the formation of imprinted binding sites to the surface of a polymer or to a very thin polymer layer with thickness comparable to the size of the protein template. The immobilization of the protein through a self-assembled anchor layer offers additional advantages over polymerization from a protein-monomer mixture in terms of generating uniformly accessible binding sites. Herein, we propose a new method to prepare Rab7 protein oriented surface-imprinted nanoporous silicon photonic crystals (PhCs) with high template utilization efficiency. Nanoporous silicon PhCs are prepared by controlled electrochemical etching of silicon and subjected to thermal oxidation generating SiO_2 to aid surface modification[3]. A His-tag is used as the anchor to facilitate the protein immobilization/removal, by exploiting a 3-step protocol functionalization of PhC surface involving i) SiO_2 silanization with glycidoxypropyltrimethoxysilane (GLYMO) preliminarly reacted with iminodiacetic acid (IDA); ii) Ni^{2+} attachment by complexation with IDA; iii) Rab7 anchoring due to strong interaction between histidine residues and Ni^{2+}. Rab7 is used as target molecule as it is a small GTPase belonging to the Rab family with a key role on different cellular pathways and processes[4]: it is fundamental for lysosomal biogenesis, positioning and functions, and for trafficking and degradation of several signaling receptors. Furthermore, Rab7 has specific functions in neurons. Each step of PhC functionalization is monitored by Visible reflectance spectroscopy. Fourier transform of each spectrum affords a peak proportional to effective optical thickness (EOT) of the porous layer[3], which is used as analytical signal for monitoring successful functionalization event. Also, protein removal by EDTA and reversibility of functionalization process is checked by determining EOT values. The developed protocol for anchoring his-tag Rab7 protein represents the preliminary step of Rab7 imprinting process, which involves subsequent self-polymerization of dopamine to control the imprinted shell thickness, protein removal by EDTA and rebinding tests monitoring the optical behavior of MIP on PhC, including its imprinting efficiency and selectivity.

References

1. C. Malitesta, E. Mazzotta, R.A. Picca, A. Poma, I. Chianella, S.A. Piletsky; *Anal. Bioanal. Chem*., 2012, 402, 1827.
2. J. Erdossy, V. Horváth, A. Yarman, F.W. Scheller, R.E. Gyurcsányi; *Trend Anal. Chem*., 2016, *79*, 179.
3. S. Mariani, L.M. Strambini, G. Barillaro; *Anal. Chem*., 2016, *88*, 8502.
4. F. Guerra, C. Bucci; *Cells*, 2016, *5*, 34.

A Novel Biosensor Based on Chemiluminescent Lateral Flow Immunoassay Integrated with Amorphous Silicon Photodiodes for Quantitative Detection of Human Serum Albumin

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Paper-based biosensors are emerging analytical tools for rapid on-site detection of clinical biomarkers in complex matrices, thanks to their ease of use and low cost. In this context, Lateral Flow Immunoassay (LFIA), a technology widely applied in resource-poor or non-laboratory environments, is based on prefabricated strips of a carrier material containing dry reagents that are activated by applying the fluid sample. LFIAs are mostly available for qualitative analyses exploiting naked eye observation of color signals due to a colloidal gold tracer. Recently, we reported LFIAs exploiting enzyme tracers and chemiluminescent (CL) detection to obtain quantitative information and reach high detectability[1,2]. Additionally, thin film hydrogenated amorphous silicon (a-Si:H) photodiodes[3,4] have been recently proposed as a low-cost and versatile technology for developing miniaturized biosensors with high degree of integration and providing high assay detectability and sensitivity. Herein, we report the development of a CL-LFIA-based biosensor with integrated a-Si:H photosensors array to quantitatively detect human serum albumin (HSA) in urine samples. The analytical method is based on an indirect competitive immunoassay using horseradish peroxidase (HRP) as a tracer and a luminol/enhancer/hydrogen peroxide cocktail for CL detection. The system is composed of a PDMS cartridge that houses the LFIA strip and all the reagents necessary for the CL immunoassay and that is aligned with an array of a-Si:H photodiodes deposited on a glass substrate. During the LFIA analysis, the photodiodes are employed to acquire the CL signals, through a custom portable electronics equipment. The method is simple and fast with a detection limit of 3 mg L^{-1}. It provides quantitative analysis in the range of 3-230 mg L^{-1} which is suitable for measuring physiological levels of HSA in urine samples and their variation in different diseases. The analytical performances of this method were compared with those obtained using a charge-coupled device (CCD) as detector. The use of CL detection allowed accurate and objective analytes quantification in a dynamic range that extends from nanomoles to micromoles. Based on these results, it was demonstrated that the integration of the a-Si:H photosensors array with CL-LFIA technique provided a compact, sensitive and potentially low-cost microdevice for chemiluminescence and bioluminescence-based bioassays with a wide range of possible applications for in-field and point-of-care bio-analyses.

References
1. M. Zangheri, F. Di Nardo, L. Anfossi, C. Giovannoli, C. Baggiani, A. Roda, M. Mirasoli; *Analyst*, 2015, 140, 358-365.
2. M. Zangheri, L. Cevenini, L. Anfossi, C. Baggiani, P. Simoni, F. Di Nardo, A. Roda; *Biosensors and Bioelectronics*, 2015, *15*, 63–68.
3. M. Mirasoli, A. Nascetti, D. Caputo, M. Zangheri, R. Scipinotti, L. Cevenini, G. de Cesare, A. Roda; *Anal. Bioanal. Chem*., 2014, 406, 5645-5656.
4. D. Caputo, G. de Cesare, L.S. Dolci, M. Mirasoli, A. Nascetti, A. Roda, R. Scipinotti; *IEEE SENSORS JOURNAL*, 2013, 13, 2595 – 2602.

Optimizing The Electrodeposition Protocol Of Enantioselective Inherently Chiral Electrode Surfaces: A Profilometry Investigation

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In our current research on enantioselective voltammetry on chiral electrodes based on electrodeposited enantiopure inherently chiral oligomer films, after achieving the first proof of concepts[1-5], we are currently concentrating on key issues such as optimizing the deposition protocol to enhance performances and improve reproducibility, as well as looking for interpretative/predictive guidelines concerning the observed enantioselection phenomena.

To this aim we are carrying out *inter alia* a systematic profilometry investigation of chiral film surfaces electrodeposited from two different chiral monomers according to a carefully optimized protocol, studying the effect of key experimental parameters such as the underlying electrode support, the deposition medium, the potential scan rate and the deposition cycle number, also comparing films obtained from enantiopure monomers with racemate ones.

The interesting results will be presented and discussed, also in connection with the electrode enantioselection performance.

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References
1. *Angew. Chem. Int. Ed.*, 2014, *53*, 2623.
2. *Chem. Eur. J.*, 2014, *20*, 15298.
3. *Chem. Sci.*, 2015, *6*,1706.
4. *Chem. Eur.*, 2016, *22*,10839.
5. *Anal. Bioanal. Chem.*, 2016, *408*, 7243.

Potentiometric Sensor for Non Invasive Lactate Determination in Human Sweat

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The present work describes a non invasive lactate sensing in sweat during workout. The sensing system is based on a non-equilibrium potentiometric measure performed using disposable, chemically modified, screen printed carbon electrodes (SPCEs) that can be wetted with sweat during the exercise. The potentiometric signal, which is proportional to lactate concentration in sweat, is produced by a redox reaction activated by UV radiation, as opposed to the enzymatic reaction employed in traditional, blood-based measuring devices. The sensing system exhibits chemical selectivity toward lactate with linearity from 1 mM up to 180 mM. The dynamic linear range is suitable for measurement of lactate in sweat, which is more than 10 times concentrated than hematic lactate and reaches more than 100 mM in sweat during workout. The noninvasive measure can be repeated many times during exercise and during the recovery time in order to get personal information on the physiological and training status as well as on the physical performance.

The device was successfully applied to several human subjects for the measurement of sweat lactate during prolonged cycling exercise. The lactate concentration changes during the exercise reflected the intensity of physical effort. During the exercise sweat was simultaneously sampled on filter paper and extracted in water, and the lactate was determined by HPLC for method validation. This method has perspectives in many sport disciplines as well as in health care and biomedical area.

Antibody Powered Nucleic Acid Release Using A DNA-Based Nanomachine

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Inspired from transport proteins, highly evolved machines that are essential to the crucial mechanism of cell transport, we rationally designed here a new class of DNA-based nanomachines that can reversibly load and release a molecular cargo upon the binding to a specific target antibody. Our strategy to rationally design an antibody-driven DNA-based nanomachine involves the use of a triplex forming DNA strand that is designed to recognize a specific DNA strand through the formation of a clamp-like triplex forming mechanism involving both Watson-Crick and Hoogsteen interactions and which is conjugated at the two ends with a pair of antigens[1]. Antibody binding to the two antigen tags in the nanomachine causes a conformational change that energetically disrupts the triplex-forming Hoogsteen interactions in the triplex complex thus destabilizing the nanomachine/cargo complex. The design principle for antibody-powered release of a molecular cargo strand is highly generalizable and can easily be adapted to other antibodies via the expedient of changing the recognition element employed. We have demonstrated here that our approach can be extended to different triggering antibodies and the effect can be specific and selective enough even in complex media (90% serum). Given these attributes, the antibody-poweered DNA nanomachines we have developed here may prove of utility in a range of applications, including point-of-care diagnostics, controlled drug-release and in-vivo imaging.

Reference
1. Ranallo S, Prévost-Tremblay C, Vallée-Bélisle A, Ricci F. Antibody powered nucleic acid release using a DNA-based nanomachine. Nat. Comm. 2017, DOI: 10.1038/ncomms15150.

Green Chemical Approaches toward High-Quality semiconductor thin film by Electrochemical Atomic Layer Deposition

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The Electrochemical Atomic Layer Deposition (E-ALD) is a green technique that allows to produce thin films of semiconductor. Exploiting Surface Limited Reactions (SLR), it enables the deposition of highly ordered ultra-thin films from diluted aqueous solutions and at room temperature and pressure. Underpotential deposition (UPD)[1] is a type of electrochemical SLR, where an atomic layer of a first element is deposited on a second, at a potential prior to (under) that needed to deposit the first element on itself, so that the resulting deposit is generally limited to an atomic layer. It occurs when the depositing element is able to somehow interact with the substrate, so that the deposition of the layer in direct contact with the substrate occurs at a potential preceding bulk deposition, that is, the deposition of the element on itself.

E-ALD enables the grow of ultra-thin films and 2D structured materials of interest in the fields of the nanoelectronics to new solar energy materials.

In the study presented here, E-ALD was used to grow transition metal chalcogenides. Central in the method is the necessity of singling out the proper electrochemical conditions which need to be used for deposition, namely potentials, reactants, electrolytes and pH. These are strictly dependent on the compound one wants to form on the substrate used.

The electrochemical conditions necessary to form ultra-thin films transition metal chalcogenides are described here and a miniaturized electrochemical flow cell. Here We presents also preliminary results of a structure characterization By SXRD at the ESRF.

Reference

1．D. M. Kolb, D. M., in Advances in Electrochemistry and Electrochemical Engineering, H. Gerischer and C. W. Tobias, Eds. John Wiley, Vol. 11, p 125, New York, (1978).

Tunable Growth Of Gold Nanostructures At PDMS Surface To Obtain Plasmon Rulers With Enhanced Optical Features

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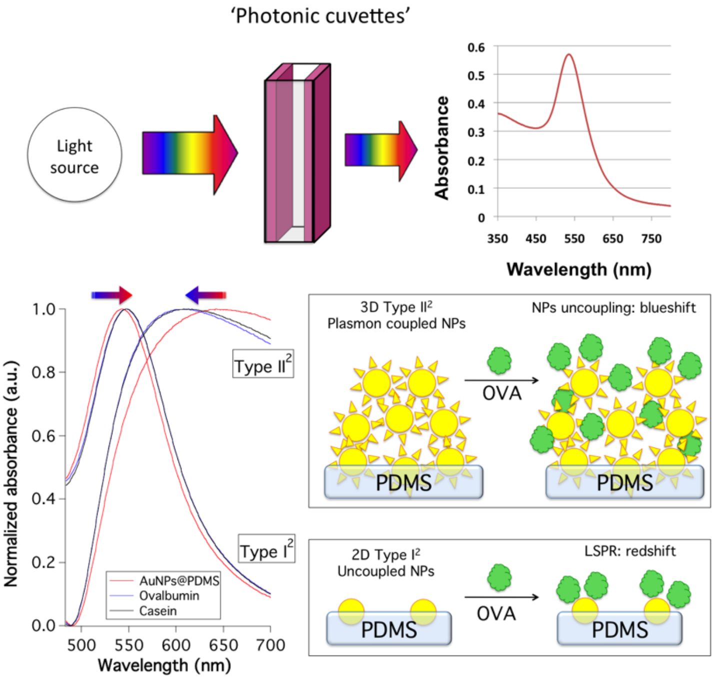
Efficient coupling of plasmonic nanomaterials to optically transparent polymers still is a challenge in order to obtain affordable, versatile, and sensitive surface plasmonic devices. The *in-situ* fabrication of gold and silver nanoparticles on PDMS has been reported, but the resulting bulk sensitivities (of up to 70 nm RIU- 1) may still be improved. The authors report that few simple modifications to the general preparation of these composites (AuNPs@PDMS) can result in substantial improvements of the optical features. A two-steps growth of AuNPs@PDMS is found to be particularly effective. It includes chemical treatment of the PDMS surface before the formation of well-exposed and densely-packed 3D conglomerates of gold spheroids with enhanced bulk sensitivity. Differently from available approaches, the structures obtained by this method display sensitivity to refractive index change of about 250 nm RIU-1. This is 3.5 times higher than spherical nanoparticles prepared by similar protocols and is near the optical performance of anisotropic NPs. Due to the strong 3D character of the structures, excellent plasmon coupling is realized on PDMS surface. The authors also show that these nanocomposite substrates can be subjected to external stimuli and then exhibit red shifts or blue shifts typical of induced plasmon coupling and uncoupling. Hence, the method represents a major step forward in terms of high- performance composite plasmonic nanomaterials for use in biosensing.



Synthesis of Xylitol-stabilized gold nanoparticles: a quantitative and sensitive method for xylitol detection in oral fluid by means of colorimetric assay

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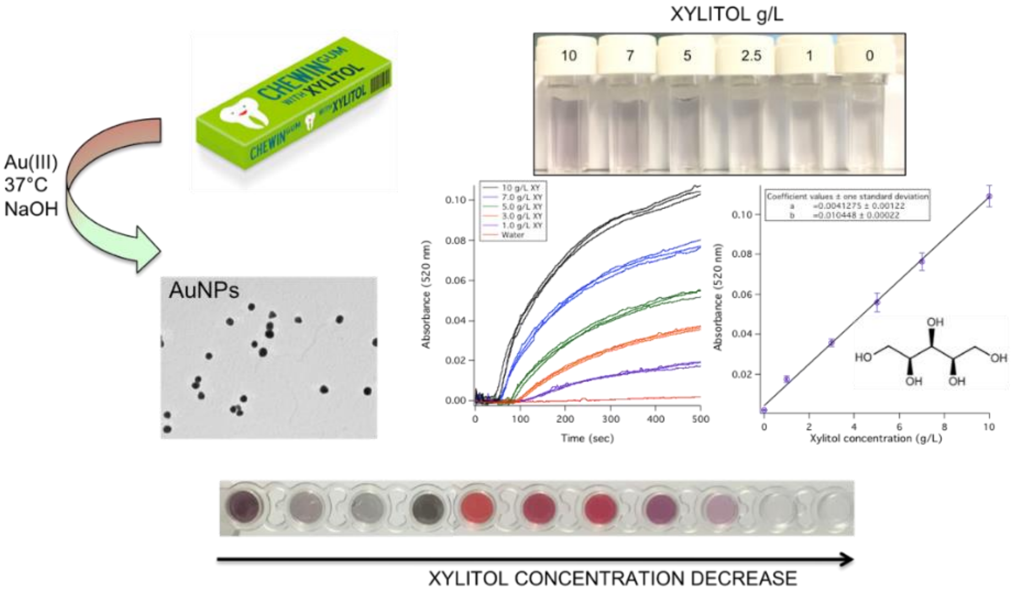
Here we present the controlled synthesis of xylitol-stabilized gold nanoparticles (AuNPs) for the sensitive and reproducible detection of xylitol in oral fluid. The optical detection is achieved by following the early stage kinetic formation of gold nanoparticles at fixed wavelength by spectrophotometry. In fact, Xylitol in alkaline solution is able to induce the fast reduction of Au(III), which leads to highly stabilized and spherical AuNPs suitable for colorimetric assays.

Xylitol is an assessed anticariogenic agent, safe and effective in controlling dental caries[1]. Therefore, the detection of minimal salivary levels of this polyol along time is crucial to set up effective administration[2].

Traditionally, the quantitative detection of xylitol in saliva/oral fluid is carried out by commercially available enzymatic tests, cost and time expensive.

The sensitivity of the developed approach is comparable to enzymatic test, but allows to get quantitative results in minutes, in a cheap and green manner. The coefficient of variation is ~7% within the calibration range, i.e. 10-1 mg/mL, with an estimated detection limit of ~80 mg/L both in standard samples and in real oral fluid.



Ethanol Determination In Several Pharmaceutical Tinctures, Using New Enzymatic (Or Not Enzymatic) DMFC Devices And Comparison With A Conventional Catalase Biosensor, Considered As Reference Method.

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In previous research[1,2], we investigated the possibility to utilize Direct Methanol Fuel Cell (DMFC), both enzymatic or not enzymatic, for analytical purposes[1]. Our research group has now continued the analytical research, devoted to the use of this enzymatic and not enzymatic Fuel Cell. The research reported in this communication concerns the possibility to check, in a simple and inexpensive way, the ethanol content of several pharmaceutical tinctures using the enzymatic, or not enzymatic DMFC device. In this case the obtained results have been compared both with the ethanol content declared by the producer firms and with data obtained analyzing the same samples using an amperometric catalase enzyme sensor, recently pointed out in our laboratory[2], considered as reference method. The purpose of the present research was to determine the concentration of ethanol in five different mother tinctures for pharmaceutical use, by means of three different sensor methods: one using a classic amperometric biosensor, based on the catalase enzyme, already previously tested[3], and the other two, that use, for analytical purposes, a small direct methanol fuel cell (DMFC), however, one of the latter two, uses not only the DMFC cell, but also the alcohol dehydrogenase enzyme immobilized and inserted into the fuel cell. These three sensor methods were compared, from the analytical point of view, by determining the concentration of ethanol contained in five different mother tinctures for pharmaceutical use. First of all, the full analytical characterization of three sensors was performed. After this analytical characterization, five pharmaceutical tinctures, containing ethanol, purchased at common drugstores, were analyzed. The nominal values were provided by pharmaceutical companies. The results obtained were then processed with two statistical tests (F-test and t-test) to compare them from the point of view of precision (F-test) and "accuracy" (t-test). In conclusion, an application on real pharmaceutical samples was shown, for which the consistency between the values found experimentally with the "fuel cell" and the nominal values (provided by the pharmaceutical companies), generally obtained by official methods (titrimetric, chromatographic, etc.), has always proved to be good (as evidenced by the t-test). Also, the concordance among the values obtained with catalase enzymatic biosensor, nominal values and those found with the fuel cell has been satisfactory. Finally, the correlation between the enzymatic and the non - enzymatic "fuel cells" was also good, but the introduction of the enzyme alcohol dehydrogenase was positive, as it increased the calibration sensitivity of the method and, above all, it drastically decreased the response time and hence the time of individual measurement. In addition, the life-time of the non-enzymatic "fuel cell", in the conditions in which it was used, proved to be extremely long, compared to the life-time of a classical biosensor, such as catalase biosensor. While that of the latter was virtually the same as that of the "fuel cell" with the addition of the enzyme alcohol dehydrogenase. Conversely, the selectivity towards the different alcohols was better for the catalase enzymatic biosensor. Finally, the data obtained with three sensor methods in the applications on the real samples were mutually correlated, as demonstrated by the good values of the obtained R^2.

References

1. Tomassetti M., Angeloni R., Merola G., Castrucci M., Campanella L.; *Electrochim. Acta*, 2016, *191*, 1001-1009.
2. Tomassetti M., Merola G., Angeloni R., Marchiandi S., Campanella L.; *Anal. Bioanal. Chem*., 2016, *408*, 7311-7319.
3. Angeloni R., Tomassetti M., Castrucci M., Campanella L.; *Curr. Anal. Chem.*, 2015, *11*, 56-67.

A Smartphone-Based Biosensor for Ultrasensitive Chemiluminescent-Lateral Flow Immunoassay for the Quantification of Ochratoxin-A in Wine and Istant Coffee

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Ochratoxin A (OTA) is a mycotoxin produced by several species of *Aspergillus* and *Penicillium* fungi that is detected worldwide in various food and feed sources. Since OTA represents a potential hazard for human health, the European Community (EC) has established a maximum level for OTA in various feed and foods, in particular 2 μg L^{-1} in grape juices, wine and must and 10 μg L^{-1} in instant coffee. Several instrumental analytical methods are currently available for detecting these toxins in foodstuff, but they require complex sample preparation and dedicated laboratory equipment. Biosensors are very promising analytical tools for rapid on-site detection of analytes in complex matrices. We recently described a biosensor for multiplex detection of type-B fumonisins and B1 aflatoxin in maize samples based on a chemiluminescence Lateral Flow ImmunoAssay (CL-LFIA) coupled with a portable ultrasensitive CCD-based "contact" imaging device[1]. The use of CL detection allowed accurate and objective analytes quantification, down to picomoles, rather than qualitative or semi-quantitative information usually obtained employing conventional LFIAs based on colloidal gold labelling. Recently, thanks to the technological advance in complementary metal oxide semiconductor (CMOS) camera technology, smartphones are emerging as detectors suitable for CL-based bioassays[2]. Here, we report on the development of a smartphone-based simple, rapid and accurate biosensor based on CL-LFIA method for quantitative detection of OTA in wine and instant coffee. The biosensor is based on a direct competitive immunoassay employing horseradish peroxidase (HRP)-OTA conjugate as a tracer, which is detected by adding the luminol/enhancer/hydrogen peroxide CL cocktail and by using a smartphone's camera for image acquisition and data handling. A self-standing microfluidic cartridge was developed, which houses the LFIA membrane and all the reagents necessary for the analysis. For CL signal detection, a smartphone cover-like adaptor, containing a plano-convex lens aligned with the camera, was developed and produced by 3D printing. Once the operator has carried out the assay using the LFIA cartdridge, both the smartphone and the cartridge are assembled with the smartphone adapter creating a mini-dark box to perform measurement of the CL signal. Calibration curves were generated by adding known amounts of OTA standard solutions to wine and instant coffee OTA free founding a limit of detection of 0.3 μg L^{-1} in wine and 1.0 μg L^{-1} in instant coffee and dynamic ranges were respectively 0.3-50 μg L^{-1} and 1.0-56 μg L^{-1}. The developed system is suitable for screening procedures aimed at the quantitative detection of OTA in wine and instant coffee samples complying with EC legislation requirements.

References
1. M. Zangheri, F. Di Nardo, L. Anfossi, C. Giovannoli, C. Baggiani, A. Roda, M. Mirasoli, Analyst 140 (2015) 358-365.
2. M. Zangheri, L. Cevenini, L. Anfossi, C. Baggiani, P. Simoni, F. Di Nardo, A. Roda, Biosensors and Bioelectronics 64 (2015) 63-68.

Development of a Chemiluminescent Immunoassay for Detecting ATP, as a Biomarker of Extant Life in Planetary Explorations

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Several studies reported the presence of organic compounds in extraterrestrial environments, thus one of the main objectives of the research in the field of exobiology is the search for organic molecules and compounds in planetary exploration missions and the identification of their biological or non-biological origin. Thus several research activities are dedicated to the development of devices capable of in-situ analyzing material samples in search of organic molecules, amino acids, nucleic acids, polysaccharides and other molecular systems characteristic of organized biological systems. An important example is given by the development of the Life Marker Chip (LMC)[1].

The increasing development of extremely compact systems relying on microfluidics, commonly known as lab-on-chip (LOC) devices, has gained much attention thanks to their favorable characteristics in terms of reduced size and weight, amenability to automation, very low sample and reagent consumption, reduced analysis time and, often, superior achievable performances in terms of limits-of-detection. Thus, LOC devices are extremely suitable for space missions and are under investigation in view of future planetary exploration.

Herein, we report about the development of a competitive immunoassay based on chemiluminescent (CL) detection for the identification of Adenosine triphosphate (ATP), which is commonly accepted as a high ranking biomarker of extant life in extraterrestrial environments. It is known that CL-based detection allows developing bioassays characterized by high detectability and sensitivity and it is also particularly suited for miniaturized analytical devices, as it avoids the need for external radiation sources and complex optical systems combining filters and lenses[2]. The immunoassay will be implemented into a portable device that is being developed exploiting a microfluidic network based on capillary forces for the handling of samples and reagents, integrated with an array of thin film hydrogenated amorphous silicon (a-Si:H) photosensors for the detection of the analytical chemiluminescent signal[3]. The implementation of the CL bioassay into the compact and fully-integrated device will provide a new analytical platform for the multiparametric detection of bio-organic molecules outside of the Earth.

References

1. Sims M. R., Cullen D. C., Rix C. S., Buckley A., Derveni M., Evans D., Holm N.; *Planetary and Space Science*, 2012, *72*(1), 129-137.
2. Mirasoli M., Guardigli M., Michelini E., Roda A.; *Journal of Pharmaceutical and Biomedical Analysis*, 2014, *87*, 36-52.
3. Mirasoli M., Nascetti A., Caputo D., Zangheri M., Scipinotti R., Cevenini L., Roda A.; *Analytical and Bioanalytical Chemistry*, 2014, *406*(23), 5645-5656.

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Inorganic Components and Redox Behaviour as "Fingerprint" Of Italian Extravirgin Oil

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High quality olive oil, virgin and in particular extra virgin olive oil, are appreciated by consumers for both health benefits and pleasant flavour. Italy is by far the first country in Europe in terms of number of Protected Designation of Origin (PDO) oils, which usually relates consumers to a warm feeling of tradition, and thus to higher quality standards. Quality control issues are mainly related to a lack of sufficiently-powerful analytical methods, but also to a non objective classification of olive oil (OO), in particular related to the distinction between virgin oil (VO) and extra-virgin oil (EVOO). To support and reinforce the promotion, the valorisation of PDOs has also been suggested to increase the competitiveness of a country like Italy at international level. To modify such a scenario a strong scientific background is required, to emphasize all the different aspects related to high-added-value EVOO, such as quality, authenticity, and health benefits. This work is focused on target chemicals with high information valence in the direction of authentication, safety and product valorization by a detailed characterization of quali-quantitative inorganic profiling in EVOOs coming from different Italian regions[1]. The presence of metals in edible oils may be due to different factors: the metals can be incorporated into the oil from the soil or be introduced during the manufacturing of the foodstuff. Therefore, it can be assumed that the trace elemental distribution in olive oils varies according to their origin and then it can be supposed that a suitable statistical treatment on trace element data could allow a geographical characterization of different OOs. The total element content has been determined after pretreatment by acid digestion. An experimental design has been performed to optimize the conditions for the sample pretreatment, since a great variability was initially observed among the replicates for the same oil. When accepted value of relative standard deviations (< 10%) were obtained, a certified material and ten EVOOs from different Italian regions were analysed. The concentration of the inorganic elements at trace and ultra-trace levels using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) has been determined[2]. Moreover, electrochemical properties of EVOOs have been investigated by voltammetry. For this purpose, carbon paste electrodes (CPE) were made mixing graphite powder and an aliquot of each sample; then, square-wave-voltammetry profile was registered for each CPE in a 0.1 M HCl solution. The features observed in the voltammograms reflect the reactions of electroactive compounds (such as polyphenols), which are present in the virgin olive oils mixed with the carbon paste matrix. For this reason, the voltammetric responses of the electrodes are specific for each type of oil[3]. Finally, chemometric treatments of the results were performed to assess the possibility to distinguish the region of provenience of each EVOO on the base of metal content and/or current registered during voltammetric analysis.

References
1. Angioni A. et *al.*; *Food Chemistry*, 2006, *99*, 525.
2. Llorent-Martínez E.J. et *al.*; *Food Chemistry*, 2011, *127*, 1257.
3. Apetrei C. et *al.*; *Sensors and Actuators B*, 2007, *121*, 567.

Quantificazione Di Caffeina Ed Acido Clorogenico Nei Chicchi Di Caffè Verde Mediante HPLC-DAD E Chemiometria

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Una procedura cromatografica basata su un gradiente di separazione rapido è stata combinata con il metodo chemiometrico di deconvoluzione di segnali Multi Curve Resolution-Alternating Least Squares, (MCR-ALS)[1-3] al fine di quantificare la caffeina e l'acido clorogenico presenti nei chicchi di caffè verde. Sono state seguite due differenti procedure al fine di ottenere gli estratti da analizzare mediante HPLC-DAD; in entrambi i casi i chicchi sono stati polverizzati ed in seguito, l'estrazione ha avuto luogo mediante acqua o mediante miscela di solventi (metanolo/acqua). Dopo l'aggiunta dello standard interno (4-nitroanilina), gli estratti sono stati iniettati in HPLC (fase debole: acqua milli-Q acidificata con acido formico, fase forte: metanolo acidificato con acido formico allo 0.1%). Nonostante i tempi della corsa cromatografica non fossero sufficienti per una effettiva risoluzione dei picchi relativi alle sostanze presenti nei chicchi di caffè verde, la successiva analisi chemiometrica ha permesso la loro deconvoluzione e, di conseguenza, la creazione di una retta di calibrazione mediante la quale i due composti di interesse (caffeina ed acido clorogenico) sono stati quantificati. In una seconda parte dello studio, è stata valutata la possibilità di classificare, mediante Partial Least Squares Discriminant Analysis (PLS-DA)[4] e Soft Independent Modeling of Class Analogies (SIMCA)[5-6] i campioni sulla base della diversa cultivar dei chicchi (Arabica o Robusta). Utilizzando SIMCA come metodo di classificazione, i risultati migliori sono stati conseguiti sui dati ottenuti mediante estrazione con miscela di solventi, raggiungendo una sensitività ed una specificità del 100% per entrambe le classi. Costruendo i modelli di classificazione con PLS-DA, si è ottenuta una corretta classificazione del 100% indipendentemente dalla procedura utilizzata per l'estrazione. A scopo di esempio, in Figura 1 sono stati riportati i risultati relativi alla classificazione mediante PLS-DA (Figura 1a), e SIMCA (Figura 1b ed 1c) relativi ai campioni estratti mediante miscela di solventi.

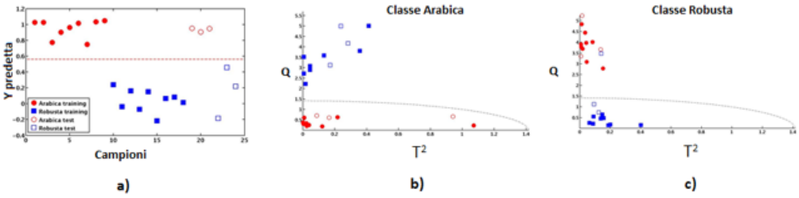

Figura: 4 Predizioni relative ai modelli: a) PLS-DA; b) SIMCA per la classe Arabica; c) SIMCA per la classe Robusta

References
1.de Juan A, Rutan SC, Maeder M, Tauler R. MCR chapters. In: Brown S, Tauler R, Walczak B, editors. Comprehensive chemometrics, vol. 2. Amsterdam: Elsevier; 2009. p. 207–558.
2.de Juan A, Tauler R. Multivariate curve resolution (MCR) from 2000: progress in concepts and applications. Crit Rev Anal Chem 2006;36:163–76.
3. Tauler R. Multivariate curve resolution applied to second order data. Chemom Intell Lab Syst 1995; 30:133–46. I. E. Frank and B. R. Kowalski, Prediction of wine quality and geographic origin from chemical measurements by Partial Least-Squares regression modeling, Anal. Chim. Acta, 162 (1984) 241–251.
4. M. Barker, W. Rayens, Partial least squares for discrimination, J. Chemometr.2003, 17, 166-173.
5. S. Wold, Pattern Recognition by means of disjoint principal components models, Pattern Recognit. 1976, 8, 127-139.
6. S. Wold, M. Sjöström, SIMCA: a method for analysing chemical data in terms of similarity and analogy. In: Kowalski, B.R. (Ed.) Chemometrics, Theory and Application, American Chemical Society Symposium Series No. 52, American Chemical Society: Washington, DC, 1977, 243-282.

Caratterizzazione Di Ossa Fossili Provenienti Da Salme Sottoposte o Non A Cremazione Mediante Spettroscopia NIR, Analisi Termica e Chemiometria

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Dei reperti di ossa fossili (24 campioni) provenienti da quattro diverse necropoli, due in Italia (Cava degli Zucchi ed Elia-Velia) e due in Sudan (El Geili e Saggai) sono stati analizzati mediante analisi termica (termogravimetria) e spettroscopia NIR. Le misure termogravimetriche sono state effettuate sui campioni triturati, mentre l'analisi spettroscopica ha permesso di non modificare (e distruggere) i campioni. Le informazioni ottenute mediante le diverse tecniche sono state confrontate al fine di poter evidenziare e studiare eventuali differenze tra i reperti provenienti dalle diverse necropoli. L'interesse della comparazione risiede nel fatto che i campioni provenienti dall'Africa (non solo differiscono per l'origine), ma hanno subito anche una diversa sepoltura, che non prevedeva la cremazione dei corpi, che invece è stata praticata sui reperti provenienti dalle due necropoli site in Italia. I reperti risalgono ad epoche storiche differenti; romanica/preromanica quelle italiane, di epoca preistorica, meroitica e cristiana quelle sudanesi. Eventuali differenze/somiglianze all'interno del set di dati sono state investigate estraendo l'informazione presente in esso mediante l'Analisi delle Componenti Principali (PCA)[1-3]. A tal fine, i modelli PCA sono stati calcolati sulle matrici individuali (spettri NIR e termogrammi) ed in un'analisi congiunta (*multi-block*), calcolando il modello PCA sulla matrice dei *super-scores* ottenuta concatenando le componenti estratte dai modelli individuali. L'investigazione degli scores plot così ottenuti ha permesso di evidenziare alcuni raggruppamenti all'interno del data set. In particolare, la prima componente principale permette di distinguere i reperti sulla base del rito funebre praticato, infatti, i campioni cremati cadono a valori positivi della prima PC1 mentre gli altri a valori negativi. La seconda componente è connessa all'informazione relativa all'epoca a cui risalgono i reperti. Infatti, i campioni più antichi, cioè di tipo preistorico, si presentano a valori elevati di PC2, i campioni di epoca romana/preromana si trovano intorno allo zero della seconda componente principale ed i campioni cristiani cadono a valori negativi della PC2.

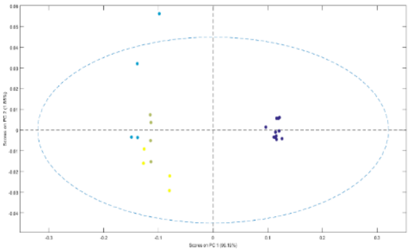

Figura 5 Scores Plot del modello PCA calcolato sui dati ottenuti mediante analisi termica. Legenda: in blu campioni cremati, in celeste campioni non cremati risalenti all'era preistorica, in verde e giallo campioni non cremati risalenti rispettivamente all'epoca meroitica e cristiana.

References
1. I.T. Jolliffe, Principal Component Analysis, 2a ed., Springer, New York, Stati Uniti, 2002.
2. K. Parson; "On lines and plans of closes fit to systems of points in space"; *Philosophical Magazine*, 1901, *2*, 559-572.
3. S. Wold, K. Esbensen, P. Geladi; Principal component analysis, Chemometrics and Intelligent Laboratory Systems; 1987, *2*, 37-52.

Locally Weighted SO-PLS

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L'affinarsi delle moderne strumentazioni per l'analisi chimica ha permesso, soprattutto negli anni più recenti, che sempre più comunemente ci si trovi a dover analizzare i cosiddetti *multi-block data set*, ovvero, set di dati estratti dalle stesse matrici mediante diverse tecniche analitiche. I metodi di regressione multi-block sono stati sviluppati al fine di effettuare delle predizioni a partire da due o più blocchi di variabili indipendenti. In letteratura sono stati presentati diversi procedimenti per effettuare l'analisi dei dati mediante *data-fusion*; in diversi lavori è stata evidenziata l'efficacia delle metodologie multi-block rispetto all'analisi individuale di ogni singolo set di dati. Un altro effetto del progredire della tecnologia è la possibilità di ottenere dei dati sempre più complessi ed informativi. Questa caratteristica, che rappresenta indubbiamente un vantaggio, fa però sì che tutti gli effetti provenienti da diverse fonti di varianza, compresi effetti moltiplicativi indesiderati e noise strumentali non linearmente correlati con i fenomeni di interesse, siano più marcati. Di conseguenza, non sempre è possibile utilizzare dei metodi che siano basati su assunzioni di linearità all'interno dei dati. Nei casi in cui la non-linearità sia particolarmente evidente, è bene che i dati vengano analizzati mediante metodi sviluppati appositamente. In letteratura è possibile trovare diversi metodi elaborati al fine di risolvere problemi di dati non lineari in diversi ambiti, sia per l'analisi esplorativa che in regressione. Nonostante ci sia un notevole interesse sia per lo studio dei metodi non-lineari che per i metodi multi-block, in letteratura si trovano pochi esempi in cui questi due aspetti siano stati contestualmente investigati. Di conseguenza, lo scopo del presente lavoro è stato quello di sviluppare un metodo multi-block di regressione che permetta di analizzare dati chimici relativi a fenomeni non lineari. A tal fine, si è partiti da un metodo multi-block chiamato Sequential and Orthogonalized-PLS (SO-PLS)[1], e lo si è elaborato al fine di adattarlo all'analisi di modelli non lineari. Nello specifico, si è investigata la possibilità di creare dei modelli SO-PLS su dei sotto-gruppi dei campioni del data set, valutando localmente le distanze relative dei campioni sotto studio. Operativamente, la procedura proposta è di elaborare, inizialmente, un modello SO-PLS standard utilizzando tutti i dati presenti nel data set; in seguito, i campioni vengono proiettati nello spazio delle prime variabili latenti dei due blocchi predittivi e tutte le distanze euclidee tra i diversi campioni vengono calcolate. Di volta in volta, solo i campioni di training più vicini al campione incognito da predire sono utilizzati per la costruzione del modello multi-block; di conseguenza, ogni campione sarà predetto attraverso un differente modello locale. Sulla base di queste caratteristiche, il metodo proposto è stato chiamato locally-weighted-SO-PLS ed è stato esteso anche nell'ambito della classificazione, mediante combinazione con la Linear Discriminant Analysis (LDA)[2]. Il metodo è stato testato su diversi data sets, sia in regressione che in classificazione.

References
1. T. Næs, O. Tomic, B.-H. Mevik, H. Martens, Path modelling by sequential PLS regression, J. Chemometr. 25 (2011) 28–40.
2. R.A. Fisher, The use of multiple measurements in taxonomic problems, Ann. Eugen. 7 (1936) 179–188.

Fourier Transform Infrared Spectroscopy and Termogravimetric Analysis in the Leather Quality Control: the Project LIFETAN (LIFE14 ENV/IT/000443)

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LIFETAN project is aimed at demonstrating the use of innovative natural products and technologies in the leather tanning process. The current commercial chemicals employed in the tanning process are very toxic and have a big impact on the environment. For this reason, EU supports Life+ Program in order to replace products/processes with eco-sustainable and convenient ones to propose "green" industrial cycles.

LIFETAN implements the results obtained in five previous Life+ projects that successfully demonstrated the use of natural products in the tanning cycle: OXATAN for the tanning phase, PODEBA for bating, ECODEFATTING for defatting, ECOFATTING for the fatting phase, BIONAD for the dyeing phase. LIFETAN as well as all Life+ projects demonstrate the use of the new natural products at laboratory, semi-industrial and industrial phase. The goals are to propose products with higher biodegradability and performance to produce high quality leather products better or comparable with those obtained employing traditional ones.

Spectroscopic techniques are fundamental in the monitoring actions to characterize the leather samples. In particular FTIR is a valuable useful technique to investigate at molecular level the interaction of new products with the leather proteins. The FT-IR analysis of amide I band gives information both in terms of the absorbance ratios at two different wavelengths (e.g. the 1654/1690 cm-1 absorbance ratio to evaluate the collagen cross linking) and the analysis of the single components found by peak fitting (conformational analysis). The results obtained on several LIFETAN samples obtained with the new tanning formulations are described and compared with thermogravimetric (TGA) data.

Transparent carbon nanotube network for efficient electrochemiluminescence device

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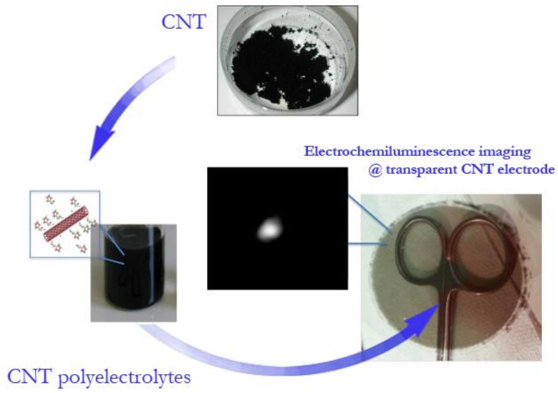
Electrochemiluminescence (ECL), or electrochemically generated chemiluminescence, is a leading technique in bioanalysis.(1) Since the excited species are produced with an electrochemical stimulus rather than with a light excitation source, ECL displays improved signal-to-noise ratio compared to photoluminescence, with minimized effects due to light scattering and luminescence background.(2) The peculiar analytical performances in terms of high detectability of conventional chemiluminescence (CL) are retained and, in addition, the electrochemical trigger of the reaction allows controlling the time and position of light emission from ECL probes. These properties make ECL systems particularly attractive also for microscopy imaging techniques in biological tissue sections or single cells, such as *in situ* hybridization (ISH) and immunohystochemistry (IHC).

In the quest for ever-increasing sensitivities, ECL can ideally be coupled to nanotechnology and supramolecular chemistry to develop new systems and strategies for analyte determination also in very complex matrices. For instance, we have recently shown a supramolecular approach to detect sarcosine, a potential prostate cancer biomarker, in urines, with good sensitivity and very high selectivity.(3) In this context, the nanostructured materials such as carbon nanotubes (CNTs) and graphene are particularly promising for sensing applications. (4)

Here we present the application of optically transparent electrodes based on carbon nanotubes and graphene based materials to ECL, (5) demonstrating the electrocatalytic superiority of such materials *vis-à-vis* ITO electrodes. CNTs and graphene electrodes are excellent material for ECL application thanks to the very favourable overpotential of amine oxidation that represents the rate-determining step for the signal generation in both research systems and commercial instrumentation. The employ of carbon nanotubes resulted in a ten times higher emission efficiency compared to commercial transparent ITO electrodes. Finally, we demonstrate as a proof of principle that our CNT device can be used for ECL imaging in which micro-beads were used to mimic a real biological sample, such as single cell visualization.



References:
1. http://www.cobas.com/home/product/clinical-and-immunochemistry-testing/technology-elecsys-ecl.html
2. a) Hu, L. Z. ; Xu, G. B. *Chem. Soc. Rev.*, **2010**, *39*, 3275-3304. b) Valenti, G.; Fiorani, A.; Li, H.; Sojic, N.; Paolucci, F.; *ChemElectroChem* **2016**, *3*, 1990 – 1997.
3. Valenti, G.; Rampazzo, E.; Biavardi, E.; Villani, E.; Fracasso, G.; Marcaccio, M.; Bertani, F.; Ramarli, D.; Dalcanale, E.; Paolucci, F.; Prodi, L. *Faraday Discuss*. **2015**, *185*, 299
4. Zamolo, V.; Valenti, G.; *et al ACS Nano*, **2012**, *6*, 9, 7989–7997.
5. Valenti, G.; Zangheri, M.; Sansaloni, S. E.; Mirasoli, M.; Penicaud, A.; Roda, A.; Paolucci, F.; *Chem. Eur. J.* **2015**, 21, 12640 – 12645.

Geographical discrimination of saffron (*Crocus sativus* L) by ICP-MS elemental data and class modelling of PDO *Zafferano dell'Aquila* produced in Abruzzo (Italy)

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Saffron, the spice obtained by drying of stigmas of *Crocus sativus* L., is the most expensive in the world and one of the most frequently adulterated foodstuffs. Therefore, certifying saffron origin and authenticity is of great economic importance, especially for the spices cultivated and entirely manufactured in given geographical areas following traditional methods, which add specificity and commercial value to the product making it competitive in the market. In the European Union, traditional specialties are valorized by means of specific regulations and marks such as the Protected Designation of Origin (PDO). Saffron cultivated near L'Aquila (Piana di Navelli), *Zafferano dell'Aquila*, is one of the five spices produced in Europe that can currently exhibit the PDO label. In the last decades, discrimination of saffron based on the geographical origin has been attempted by classification methods applied to experimental data obtained by both separative methods (HPLC and GC) and untargeted approaches (NMR, IR, UV-vis spectroscopy, among the others)[1,2]. In all the above approaches, discrimination is based on the difference in the metabolic profile, which is expected to be related with the production area and the local know-how applied in the post-harvest drying process. Trace mineral composition, on the other hand, was only rarely considered in the geographical traceability of saffron[3].

In this study, we further explore the potentiality of the elemental composition, determined by inductively coupled plasma-mass spectrometry (ICP-MS), in the geographical traceability of saffron. ICP-MS data of 52 elements collected on samples of *Zafferano dell'Aquila*, saffron samples produced in Iran, commercial products and spices cultivated in other Italian areas (Sardinia and Umbria) were preliminarily handled by unsupervised (principal component analysis) and supervised (linear discriminant analysis) multivariate methods. In addition, some class modelling techniques[4] were applied to evaluate the usefulness of the mineral composition in the authenticity verification of the PDO *Zafferano dell'Aquila*.

References

1. Anastasaki et al. Geographical differentiation of saffron by GC-MS/FID and chemometrics. Eur. Food Res. Technol. *229* (2009) 899-905.
2. Zalacain, et al. Near-infrared spectroscopy in saffron quality control: determination of chemical composition and geographical origin. J Agr. Food Chem. 53 (2005) 9337-93412.
3. D'Archivio et al. Analysis of the mineral composition of Italian saffron by ICP-MS and classification of geographical origin. Food Chem. 157 (2014) 485-489.
4. Forina et al. Class-modelling techniques, classic and new, for old and new problems. Chemom. Intell. Lab. Syst. 93 (2008).

"Spatio-spectral fuzzy-clustering" come vincolo spaziale per la risoluzione di immagini iperspettrali

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A differenza dei metodi di clustering tradizionali, nei quali ogni punto viene assegnato ad uno ed un solo gruppo, in maniera tale che tutti i punti in un cluster siano tra di loro i più simili possibile (e quanto più diversi possibile dai punti negli altri gruppi), gli algoritmi di fuzzy clustering prevedono che ogni osservazione possa appartenere a più di un cluster, associandole una probabilità per ciascuna delle attribuzioni. Per l'analisi delle immagini iperspettrali, ovvero delle immagini digitali per le quali a ciascun pixel sia associato un intero spettro, le tecniche di fuzzy clustering sono state in genere applicate considerando l'immagine come un insieme di spettri, ovvero senza prendere in considerazione l'informazione spaziale. D'altro canto, la possibilità di utilizzare l'informazione spaziale nell'ambito del fuzzy clustering è stata invece considerata nella risoluzione di immagini monocromatiche, come quelle ottenute dalla risonanza magnetica nucleare applicata nel campo del *medical imaging*[1]. Partendo da queste considerazioni, si è deciso di definire un algoritmo che permettesse di calcolare la funzione di appartenenza di ciascun pixel di un'immagine iperspettrale attraverso una procedura di fuzzy clustering che combinasse in sé l'informazione spaziale e spettrale (*spatio-spectral fuzzy clustering*). Questa procedura procede definendo una prima probabilità di appartenenza di ciascun pixel ai vari clusters sulla base della sola informazione spettrale, ed aggiornando successivamente questa probabilità sulla base della distribuzione spaziale delle funzioni di appartenenza: in questo modo, l'appartenenza di un pixel a un particolare cluster sarà tanto più probabile quanto maggiore sarà il numero di pixel vicini con alta probabilità di appartenere allo stesso gruppo. In questo contesto, obiettivo principale di questo lavoro è stato quello di verificare la possibilità di inserire l'algoritmo di *spatio-spectral fuzzy clustering* come vincolo all'interno dell'algoritmo iterativo *Multivariate Curve Resolution-Alternating Least Squares* (MCR-ALS)[2] al fine di migliorare la risoluzione spaziale delle immagini di tipo iperspettrale e rendere maggiormente evidenti ed omogenee le aree in cui le componenti di un campione siano distribuite. In particolare, si stabilisce di avere un numero di clusters uguale al numero di componenti nella risoluzione a cui applicare il vincolo e, ad ogni iterazione, si calcolano le funzioni di appartenenza per ciascun pixel sulla base della stima delle mappe di concentrazione. Queste funzioni di appartenenza vengono quindi utilizzate come pesi per calcolare una nuova stima delle mappe di concentrazione da usare nell'iterazione successiva dell'algoritmo ALS. Il procedimento viene ripetuto fino a convergenza dell'algoritmo stesso. Questo procedimento è stato applicato a due diversi campioni di emulsione, ossia una emulsione di olio di paraffina disperso in acqua ed un campione di maionese, preso ad esempio di emulsione commerciale. In entrambi i casi, l'algoritmo MCR è stato applicato utilizzando, oltre allo *spatio-spectral fuzzy clustering* oggetto di studio, il vincolo di non-negatività applicato ai profili spettrali e di concentrazione.

References
1. Chuang K-S., Tzeng H-L., Chen S., Wu J., Chen T-J., *Fuzzy c-means clustering with spatial information for image segmentation*, Comput. Med. Imaging Graph. 30 (2006) 9–15.
2. de Juan A., Jaumot J., Tauler R., *Multivariate Curve Resolution (MCR). Solving the mixture analysis problem*, Anal. Meth. 6 (2014) 4964-4976.

Fluorescence spectroscopy and chemometric techniques for geographical discrimination of green tea samples

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The geographical origin of tea samples is an important factor to determine quality and reputation of a commercial tea product. Recently, different analytical procedures have been proposed for classification of different varieties or geographical origin of teas, including HPLC, elemental analysis, UV–vis spectroscopy, Near-Infrared spectroscopy, electronic tongue, electronic nose, multispectral or hyperspectral imaging, HPLC-DAD-MS. In our previous study[1], the content of catechins and methylxanthines in 92 green tea (GT) samples originating from China and Japan was determined by using micellar electrokinetic chromatography, and pattern recognition methods were applied to discriminate GT samples according to geographical origin.

In this study, an alternative analytical approach for the geographical discrimination of the GT samples is proposed, based on the combination of excitation–emission matrix (EEM) fluorescence spectroscopy as analytical technique and chemometric tools. Excitation-emission spectra were recorded using a Perkin–Elmer LS 55 (Perkin-Elmer Ltd., Beaconsfield, UK) luminescence spectrometer, with excitation and emission slits both set at 10 nm. Emission spectra were recorded between 295 and 800 nm, at excitation wavelength ranging from 200 to 290 nm. Principal Component Analysis was used as a display method, and considering the 3-way data sets (samples, excitation and emission wavelengths) PARAFAC[2] was applied as a multi-way decomposition method in order to extract the useful information from the spectra. The classification results obtained by EEM fluorescence spectroscopy were compared with those previously obtained by using micellar electrokinetic chromatography, finding a good agreement and thus demonstrating that fluorescence spectroscopy can be considered as a promising method for classifying GT by its origin.

References
1. B. Pasquini, S. Orlandini, M. Goodarzi, C. Caprini, R. Gotti, S. Furlanetto, Chiral cyclodextrin-modified micellar electrokinetic chromatography and chemometric techniques for green tea samples origin discrimination, Talanta 150 (2016) 7-13.
2. A. Smilde, R. Bro, P. Geladi, Multi–way Analysis with Applications in the Chemical Sciences, John Wiley & Sons, New York, NY (2004).

Effects Of Cellulose Oxidative And Hydrolytic Degradation Monitoring By Infrared Spectroscopy (ATR-FTIR) With Approach Of Principal Components Analysis

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In this study, we characterize the degradation phenomena of paper by inducing an artificial ageing on the standard paper (Whatman paper, tipe 1)[1] through chemical oxidation with potassium periodate, or acid hydrolysis with exposure to acid vapors hydrochloric acid and a mix of both treatments. The artificial cellulose degradation was investigated by FTIR-ATR techniques, pH analysis, HPLC analysis and FE-SEM measurements. Finally, principal components analysis (PCA) was used to analyze the data set of the results. All performed treatments, significantly change the structure and properties of the paper; at the same time results show that the extent of deterioration depends on the kind of ageing. Furthermore, cleaning gels will be applied on aged paper samples in order to test their applicability and cleaning capability on differently aged paper artworks.

Reference
1. Manso M., S. Pessanha and M.L. Carvalho; *Atomic Spectroscopy*, 2006. *61*, 922-928.

Evaluation of penetration depth for a NIR hyperspectral system at different wavelengths and on different matrices

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Hyperspectral imaging is usually considered as a surface analysis method. Nevertheless, electromagnetic rays may penetrate in depth, inside the upper layers of the sample, including information from the inner parts in the recorded spectra. Moreover, such an effect depends on the matrices analysed and on the specific wavelengths at which spectra are recorded.

The aim of this work was the evaluation of penetration depth for a near infrared hyperspectral imaging system working in the 1000–2500 nm spectral range, at 8 nm spectral resolution (SWIR3 camera equipped with a LabScanner 40x20).

Penetration depth was evaluated on several matrices characterised by different physico-chemical features, including chemical composition, colour, humidity, and microstructure.

To the aim, a chessboard background was assembled using two polymeric materials characterised by different total reflectance values (about 0% and 90%, respectively) and with different and characteristic spectral profiles. The use of a geometrical pattern, in comparison with uniform backgrounds, adds spatial information to the penetration depth evaluation. Images were recorded placing the matrices, both sliced at different thickness and wedge-shaped, between the source and the chessboard background.

Multivariate image analysis was carried out in order to highlight both spatial and spectral features, allowing to evaluate the penetration depth. First of all, a region of interest (ROI) within the hyperspectral image, including a representative portion of the sample was selected. Then, principal component analysis (PCA) was carried out, reducing data dimensionality and removing non-useful information to confirm the level of penetration on the basis of score images.

Up to now, hyperspectral imaging has been considered basically as a reflectance method but, on the basis of these outcomes, it should be regarded as a transflectance approach in many cases, depending, in particular, on the physico-chemical characteristics of the matrix, such as the chemical composition and the physical microstructure.

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Quick Determination of Olive Oil Acidity by Voltammetry and Partial Least Square Regression

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Olive oil acidity is a key parameter routinely determined to classify and/or assess quality, freshness and economic value of the final commercial product. In a recent work[1], a novel electroanalytical approach was presented for the direct determination of acidity degree in different commercial categories of oils (extra-virgin, olive oil, lampante). Acidity levels of samples were obtained by exploiting the reduction process of oleic acid (OA), recorded by voltammetry at a platinum microelectrode, which allowed minimising most of the unwanted effects on the current-potential responses, which are typically encountered in viscous and low conducting media. Suitable conductivity of the samples was achieved by addition to oils the ionic liquid tri-hexyl(tetradecyl)phosphonium bis (trifluoromethylsulfonyl) imide $[P_{14,6,6,6}]^+[NTf_2]^-$, which acted as a supporting electrolyte. With the aim of increasing repeatability and accuracy of the voltammetric approach for the quantification of the acidity degree in extra-virgin olive oils, in which the acidity levels are very low, in the present work the application of a suited multivariate regression analysis to be coupled with the voltammetric responses was investigated.

In particular, several Italian extra virgin olive oils were sampled and measured under air-saturated conditions, both at their natural acidity content and at increasing acidity levels, obtained by adding different amounts of pure oleic acid (OA) – the main fatty acid in olive oil. Cyclic voltammetry (CV) at low scan rates was used as waveform for recording current against potential responses. Simultaneously, free fatty acid content (% FFA) was determined in the same samples using the official reference titration method.

After choosing the most suitable pre-processing for CV data, partial least squares (PLS) regression was applied on selected regions of the CV signals, as an alternative approach to the classical univariate regression. PLS allows to consider also the shape of entire current profiles and to obtain a quantitative relationship with the acidity content of samples. Models were optimised choosing the optimal complexity, in terms of latent variable (LV) number and root mean squared error in prediction (RMSEP). Validation was performed on a separate sample set.

Results suggest that the proposed procedure could be advantageously exploited for a quick, low-cost and solvent-saving analytical determinations of olive oil free acidity, employing very small sample volumes (<1 mL).

Reference

1. M.A. Baldo, P. Oliveri, R. Simonetti, S. Daniele, A novel electroanalytical approach based on the use of a room temperature ionic liquid for the determination of olive oil acidity, Talanta. 161 (2016) 881–887. doi:10.1016/j.talanta.2016.09.045.

XPS characterization of (Mo/Se) films grown by electrochemical atomic layer deposition

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The interest towards 2D materials for photovoltaic applications has grown dramatically in the last years[1]. In this field, metal dichalcogenides (MX_2) are widely studied owing to their peculiar optoelectronic properties[2]. An extremely versatile approach to develop layered MX_2 is represented by electrochemical atomic layer deposition (E-ALD), which allows the growth of thin films at ambient pressure and room temperature[3]. Recently, research about the preparation of $MoSe_2$ films by alternating the electrochemical deposition of Se and Mo onto Ag(111) substrates has been started in collaboration with University of Florence. A powerful tool for the characterization of similar materials is represented by X-ray photoelectron spectroscopy (XPS), as demonstrated in our previous works combining also morphological and (*in operando*) spectroscopic investigations[3-5]. In this communication, XPS analysis of Mo/Se multilayers is presented with a particular focus on element speciation and the influence of electrochemical deposition parameters on the final surface chemical composition of thin films.

References
1. M.-Y. Li, C.-H. Chen, Y. Shi, L.-J. Li, Materials Today 19 (2016) 322-335.
2. M.T. Dau, C. Vergnaud, A. Marty, F. Rortais, C. Beigné, H. Boukari, …, M. Jamet, Appl. Phys. Lett. 110 (2017) 011909.
3. A. Giaccherini, S. Cinotti, A. Guerri, F. Carlà, G. Montegrossi, F. Vizza, …, M. Innocenti, Scientific Reports 7 (2017) 1615.
4. E. Berretti, S. Cinotti, S. Caporali, N. Cioffi, A. Giaccherini, F. Di Benedetto, …, M. Innocenti, Journal of The Electrochemical Society, 163 (2016) D3034-D3039.
5. S. Caporali, A. Tolstogouzov, O.M.N.D. Teodoro, M. Innocenti, F. Di Benedetto, S. Cinotti, …, N. Cioffi, Solar Energy Materials & Solar Cells138 (2015) 9–16.

Mitochondrial proteome modifications due to eIF6 depletion by UHPLC-QTOF MS/MS with SWATH-MS acquisition

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Eukaryotic Initiation Factor 6 (eIF6) is an initiation factor that binds 60S ribosomal subunits and has an anti-association property, by hampering 60S premature joining to 40S. In general, eIF6 is rate limiting for tumour onset and progression. eIF6 haploinsufficient cells are normal, but not efficiently transformed in vitro. Mitochondria are the main compartments of energy production, and some lines of evidence have shown that mitochondrial alterations contribute to the development of metabolic syndrome.

To this aim, we analysed, by uHPLC-QTOF-MS/MS exploiting the SWATH-MS (Sequential Window Acquisition of all Theoretical fragment ion spectra) acquisition, the expression of mitochondrial proteome of AML-12 (non-tumourigenic murine liver hepatocytes) cell line, where eIF6 was down-regulated by shRNA, and of three different tissues from wild type and +/- mice for eIF6 (liver, muscle and brain).

The SWATH-MS acquisition method is a high throughput label-free method for protein quantitation that combines the traditional shotgun proteomics with the quantitative accuracy and reproducibility of selected reaction monitoring (SRM).

We found that depletion of eIF6 by shRNA induces profound and varied impact on mitochondrial proteome, impairing the energy production, steering the metabolism toward the up-regulation of aerobic glycolysis and the inhibition of oxidative phosphorylation.

Authentication Study Along The Production Chain Of Hazelnut Paste By ICP-MS And Multivariate Analysis

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Hazelnuts are widespread in the food industry either as whole fruits, small grains, flour or oil, to produce paste, cream and other finished products, above all in confectionery. Different hazelnut cultivars show a quite different commercial value, the cultivar "Tonda gentile delle Langhe" produced in Italy being by far the most valuable. Along the industrial production chain, hazelnuts first undergo a process of roasting to exalt their aroma, and then hazelnut paste is produced by a fine grinding of the peeled fruits.

Due to the great commercial difference between the "Tonda gentile delle Langhe" and the other cultivars, it is particularly important for the food industry the availability of tools for tracing the variety and the geographic provenance of hazelnuts and their derivatives along the production chain of the hazelnut paste.

Here, we apply elemental profiling through ICP-MS and ICP-OES in an authentication study involving the production chain of hazelnut paste: from raw fruits, to roasted hazelnuts, down to the final paste. The study involves three different cultivars ("Tonda Gentile delle Langhe", "Romana" and "Mortarella"). PLS-DA with variable selection was applied to identify a model able to distinguish the three cultivars, independently on the type of technological transformation, and to search for elemental markers of authenticity. The model performances were very good both in fitting and cross-validation and proved the applicability of the procedure for the authentication of hazelnuts along the production chain of hazelnut paste. To the authors knowledge, this is the first authentication study involving the production chain of this product.

Rare Earth Elements Analysis For Extra Virgin Olive Oil Assessment: The Case Study Of Tuscany Olive Groves, Italy

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Traceability of the food origin is important for label protection. Food fraud is a growing problem that costs the *global* food industry between $10 billion and $15 billion per year. Food ingredient fraud and economically ingredient adulteration are emerging risks, but a comprehensive compilation of information about known problematic ingredients and detection methods does not currently exist. The olive oil is in the E.U. top ten list of food at the most risk of fraud. Chemical analyses per se are not sufficient to verify olive oil authenticity except in cases of adulteration with other vegetables oil. Until now, the analytical criteria available for the international regulations on the definition of oil genuineness and quality are based on the determination of classic parameters: acidity, peroxide value, ultraviolet absorption and the fatty acid composition. The above mentioned analyses are not able to trace the origin of the olive oil.

This research project, called “GEOEVO”, started in 2016 and proposes an alternative method to evaluate the geographic origin of olive oils by determining the rare earth elements (REEs) within the soil and corresponding olive oils[1]**.** Starting from the assumption that the REEs present in the soils and substrates are uptaken by plant roots. We hypothesize that different geological substrates give a combination of REEs that characterize and influence the quality and traceability of the olive oil[2]. This study will focus on the following lithologies: (i) volcanic rocks, (ii) sandstones (iii) and limestones. The specific objectives are: (i) to find a response in the absorption spectra of rare earths in soil and in olive oil samples taken as a function of different lithologies; (ii) to identify mixtures of different olive oils (blend); (iii) to calculate a statistical probability distribution of REEs in soil and in corresponding olive oil. REEs concentration results will be analyzed by statistic techniques, ANN and PCA, to reveal if the data obtained are suitable to discriminate between olive oils from different geographical origin. Sampling of soils, olives and olive oils was carried out in ten olive groves located in Tuscany. First results were reported and discussed.

References

1. A. Pisciotta, L. Tutone, F. Saiano, Food Chemistry, (2017), 221, 1214–1220.
2. L. Tutone, F. Saiano, Atti del XXV Congresso della Divisione di Chimica Analitica della Società Chimica Italiana, (2015), P10.

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Rapid Quantification Of Biosilica In Marine Sediments By ATR And Net Analyte Signal

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A novel chemometric approach based on Net Analyte Signal (NAS) has been developed and applied to the quantification of biosilica in marine sediments.

The official method for the determination of this biogenic marker is based on a wet method[1], which involves the dissolution of the sediment in a strong alkaline environment and subsequent spectrophotometric assessment. Therefore, it is a destructive method, seriously affecting precision and accuracy of analysis; moreover, the mineralization process is matrix-dependent, involving the need for different conditions to be set-up according to the different sediment investigated.

In this work in order to overcome the troublesome traditional approach, we propose a non- destructive method for the assessment of biosilica based on ATR spectroscopy and the use standard addition approach. Sediments aliquots are desiccated at 105°C, sieved and grinded with a ball mill. Then they are split in four aliquots: the first one is the zero-added sample, while a growing amounts of pure celite as a proxy for bio-silica is added to the others. These powder samples are then directly analysed by Infrared Spectroscopy in ATR mode (ATR). ATR has the great advantages of being a rapid and non-destructive technique, requiring a little amount of sample, while the complexity of the spectra requires a smart chemometric approach to solve for quantitative information they contain in implicit form.

IR spectra are therefore elaborated by the Net Analyte Signal (NAS) algorithm[2,3] which allows to extract the contribution of the analyte from the whole signal. In this way, the problem of the matrix effect affecting spectra is solved. The Euclidean norm of the NAS signal is then used to create a pseudo-univariate standard addition model, from which the concentration of biosilica in the starting sediment is extrapolated.

In order to validate the IR method, three sediment samples collected in the Station D in Ross Sea, Antarctic, at different depth have been analysed, using both the wet method and the ATR-NAS method. Results of the two methods are in good agreement, showing that NAS can be used to successfully quantify biosilica in marine sediments using a a faster, cheaper and more universal method than the traditional one.

References
1. DeMaster J.D. (1981), Geochimica et Cosmochimica Acta 45,1715-1732.
2. Lorber A. (1986) Anal. Chem. 58,1167-1172.
3. Hemmateenejad B., Yousefinejad S. (2009), Anal. Bioanal. Chem. 349,1965-1975.

The Role of Organic Gunshot Residues In Criminal Investigation

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This work has been focused on the developement of analytical protocols able to find solutions to the critical issues of current methods in gunshot residues investigation. In particular, a method based on High Performance Liquid Chromatography hyphenated to Mass Spectrometry (HPLC-MS/MS) was considered to analyze the organic components of the gunshot residues (OGSR). In fact, sensitive and robust analytical technique is essential to face an increasing number of incidents related to firearms.

Several approaches have been considered for the collection of the commonly determined primer-metal residues from the hands and clothing including swabbing[1], lifting with an adhesive tape or stub[2], and vacuuming[3], but they did not solve critical issues related to these components that may be very challenging in such situations involving lead-less cartridge.

In order to optimize the analytic method, shooting experiments were performed to evaluate transfer of OGSR using different cartdriges fired by the same shotguns, so as to find features particles of the ammunition used.

Using LC–MS in positive electrospray ionization (ESI) mode, eleven major stabilizers found in OGSR were targeted, while three compounds in negative ionization were characterized.

The achieved results have shown that, using the results derived from the analysis of OGSR, we could be draw information for investigative purposes, to give confirmation of the hypothesis of crime, making more accurate the interpretation of the analytical results.

References

1. Yañez, Farías, Zúñiga, Soto, Contreras, Pereira, Mansilla, Saavedra, Castillo, Sáez; "Differentiation of two main ammunition brands in Chile by Regularized Discriminant Analysis (RDA) of metals in gunshot residues"; *Microchemical Journal*, 2012, 101, 43–48.
2. Gilchrist, Jongekrijg, Harvey, Smith, Barron; "Characterization of gunshot residue from three ammunition types using suppressed anion exchange chromatography"; *Forensic Science International*, 2012, *221*, 50–56.
3. Cardinetti, Ciampini, D'Onofrio, Orlando, Gravina, Ferrari, Di Tullio, Torresi; "X-ray mapping technique: a preliminary study in discriminating gunshot residue particles from aggregates of environmental occupational origin"; *Forensic Science International*, 2004, *143*, 27–46.

Forensic Examination of Black Toners In Questioned Documents By NIR Spectroscopy And Chemometrics

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The examination of questioned documents represents a fundamental step in forensic investigation as it provides information about the origin and similarities of a document to detect potential falsifications[1]. In particular, the analysis of printing toners with the aim of discriminating brands, manufactures and printers involved, is becoming very challenging as the use of office and personal laser printers and photocopying machines dramatically increased[2].

In this work, the feasibility of NIR/Chemometrics was investigated as a novel way to analyse black toners in questioned documents. Ten black toners from four manufacturers were included in this study and the acquired NIR spectra were compared in order to differentiate toners. Multivariate statistical analysis based on Principal Component Analysis (PCA) was considered to optimise the model for the identification of toners in questioned documents.

Results demonstrated the ability of NIR spectroscopy to simultaneously differentiate toners according to the brand and also to a typical composition among toners of the same manufacture. Moreover, the method proved to be not affected neither by the type of paper involved, nor by the way documents are printed suggesting to be a very promising tool to compare documents of unknown origin and allowing discrimination between them. The good experimental results show the opportunity of considering the proposed approach into procedures for forensic documents examination.

References

1. A. Braz, M. Lopez-Lopez, C. Garcia-Ruiz; "Raman spectroscopy for forensic analysis of inks in questioned documents"; *Forensic Science International*, 2013, *232*, 206–212.
2. J C. Neumann, W.D. Mazzella; Questioned Documents; Forensic Sciences, Elsevier, University of Lausanne, Lausanne, Switzerland, 2005.

Validation of an Analytical Method for the Determination Illicit Drugs in Hair Based on LC-MS/MS and Comparison of Different Extraction Methods

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In the last twenty years, hair testing has gained increasing attention and recognition as a complement to blood and urine analysis. Hair differs from other materials used for toxicological analysis, due to its large detection window which is weeks to months depending[1]. Other advantages are the easy sample collection, storage and transport. Moreover, segmental analysis of hair strands allows the determination of the historic pattern of drug use. Consequently, hair analysis of illicit drugs and medicines is currently employed to address a wide range of challenges, such as drug abuse history, workplace testing, post-mortem toxicology, therapeutic drug monitoring or drug facilitated assault (DFA) investigations. The most crucial issue facing hair analysis is the avoidance of false-positive results caused by passive exposure to the drug. For this reason, SoHT recommends that hair analysis starts with a wash step to remove external contamination[2]. The extraction of psycoactive substances from the inner of the hair is a critical point of the analytical process: different methods have been proposed[3], but most of them include a limited number of analyte. For hair incubation, the most used method is the digestion of hair matrix with NOH, alternative methods consist in the incubation of hair with methanol or ethanol for several hours, up to 18. Recently we proposed a new method[4] that uses the pressurized liquid extraction (PLE), capable to obtain good recoveries in a short time. The clean-up of the sample obtained from the PLE were carried on by dispersive-liquid liquid microexcraction (dLLME). The aim of this work is to compare our method, based to PLE-dLLME, followed by HPLC-ESI-MS / MS, with classic ones considering retention times, matrix effect and recoveries. Some samples were fortified by adding an analytical solution to the hair, as is generally done in literature (spiked method), while a fortification method was then evaluated by "soaking" capable of simulating real specimens, as analytes are introduced into the hair[5]. Finally, the methods were also compared using real samples obtained from volunteer. In this work, we carried out the determination of 21 analytes, belonging to most classes of substance abuse between classics and new drugs. The results showed that the spiked fortification is unable to simulate a real sample. The proposed method is capable of obtaining a hair extraction in a few minutes, and the validation demonstrated the suitability on real samples and a clean and less influenced sample compared to other literature methods.

References
1. Verstraete A.; Ther Drug Monitor; 2005, *150*, 119-131.
2. Cooper G.A.A. et *al*.; *Foren. Scie. Inter*., 2012, *218*(1–3), 20-24.
3. Park M. et *al*.; *J. of Chromatog B*., 2014, Vol. 947– 948, p. 179– 185.
4. Montesano C. et *al*.; *J. of Chromatogr A*, 2015, *1404*, 192-200.
5. Welch M.J. et *al*.; *Anal. Bioanal. Chem*., 2003, *376*, 1205-1211.

Chemometric Approaches for the Interpretation of Direct Biomarkers of Ethanol Consumption for Forensic Purposes

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The quantitative determination of direct ethanol metabolites – i.e. ethyl glucuronide (EtG) and fatty acid ethyl esters (FAEEs) – in hair samples represents the optimal analytical approach to identify chronic alcohol abusers. Cut-off values have been established by the Society of Hair Testing (SoHT) to interpret EtG and FAEEs results, but several confounding factors (e.g. cosmetic treatments, intra-individual variability, etc.) may alter the biomarkers' concentration in hair and their correlation with alcohol consumption, potentially leading to cut-off value crossing. As a consequence, the adoption of the traditional univariate interpretation approach is exposed to misclassification errors and misleading conclusions from forensic experts and physicians. The alternative use of multivariate data interpretation approaches is tested to infer more robust conclusions. Several likelihood ratio (LR) models were developed and validated to overcome the drawbacks of the traditional univariate approaches, that involve cut-off values in an oversimplified process of evidence evaluation. In contrast, LR approaches evaluates the evidence (E) in case of two different, and mutually exclusive, hypotheses by examining the collected data. The resulting LR values reveal the support to be delivered to the evaluated propositions and LR results can be expressed by means of verbal scales. In the present case, the first hypothesis (H1) is that the individual under examination is not a chronic alcohol consumer, while the second hypothesis (H2) states that the examined subject is a chronic alcohol misuser. The collected data include direct biomarkers of alcohol consumption (FAEEs, EtG) from more than 150 scalp hair samples of different individuals, representing both a-priori chronic and non-chronic alcohol drinkers targeted categories. The different multivariate LR models were compared and their ability to discriminate between chronic alcohol misusers from non-chronic alcohol consumers was examined. The performances of each model were evaluated in terms of correct classification rate (%) and empirical cross entropy parameters. Satisfactory reduction of information loss was finally observed, together with correct classification rates close to 100%, proving that LR validated models are able to discriminate non-chronic from chronic alcohol consumers. Similar efficiency was observed employing further multivariate data analysis strategies such as Partial Least Squares – Discriminant Analysis (PLS-DA). In conclusion, multivariate statistical approaches to the interpretation of alcohol abuse biomarkers seem to efficiently corroborate clinical evidences in the diagnoses of chronic abuse.

Chemometric Interpretation Of GC-MS Fire Debris Results

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In the sphere of fire debris investigations, the analysis of collected evidences represents the main tool to recognize the occurrence of an alleged arson. The results from GC-MS analysis performed on collected fire debris may be compared to those obtained from ignitable liquids. Different gasolines were sampled from different oil stations located within the area of the city of Turin and then analysed with the aim of evaluating the chance to effectively discriminate their different origin. The study was conducted within the collaboration between the Department of Chemistry and the Turin Fire Department. The use of various approaches of multivariate data analysis allowed us to build classification and likelihood ratio models indicating the probabilities that specific fire accelerants have been employed in real arson casework. In particular, both fresh and weathered samples at different percentages (i.e. 25%, 50%, 75%, 95%) were analysed and compared to standard mixtures (ASTM1618). Furthermore, a data set including more than 150 GC-MS analysis relative to 30 oil stations was used for multivariate analysis. The collected mass-chromatograms were, in fact, interpreted using a variety of targeted and untargeted approaches of multivariate data analysis, using both raw and semi-quantitative data. In particular, Principal Component Analysis (PCA) and N-Way strategies such as Tucker3 and Parallel Factor Analysis (PARAFAC) were employed with the goal of recognizing and discriminating the usage of different fire accelerants. More in details, Principal Component Analysis allowed to locate the fresh gasoline samples within a scores plot according to their origin, i.e. the different oil stations. Moreover, N-Way strategies were tested in order to figure out how multivariate strategies were able to assess the occurrence of fire accelerant in an arson scene. To this purpose, whole tridimensional GC-MS data collected in scan mode were compared with those obtained from different oil stations gasoline samples. Then, likelihood ratio approaches have been evaluated for the same purpose, by evaluating samples that were burnt in presence or in absence of fire accelerants with the integration of Bayesian's logic. Further development of multivariate feature-based and score-based likelihood ratio models built on the collected GC-MS spectra are in progress, too.

Mechanistic insights into the ultrasensitivie determination of iron by adsorptive voltammetry with catalytic enhancement

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The detection of iron and, subsequently, iron speciation analysis made their way into the forefront issues in chemical oceanography following the discovery that iron limits algal growth (primary productivity) in substantial areas of the oceans (first formulation of the iron hypothesis in 1990 (1)). Far fetching consequences on the carbon dioxide global cycle and, consequently, on climate change have been rapidly acknowledged (1). Nevertheless, iron detection in seawater demonstrated among the most challenging topics in inorganic analytical chemistry due to the poor solubility (picomolar to nanomolar) of iron in oxygen saturated alkaline waters.

Electrochemical techniques had already emerged since mid-Seventies as reliable methods to determine a number of trace elements in solution, employing in situ accumulation techniques to achieve the required low limits of detection. Procedures based on anodic stripping voltammetry (ASV) were firstly developed followed by methods based on cathodic stripping voltammetry (AdCSV, adsorptive cathodic stripping voltammetry). They efficiently faced the issues posed by the saline matrix and the extremely low concentrations although required of a digestion step to cancel interferences from natural organic matter. The first method for iron detection in seawater by AdCSV was introduced in 1984 by van den Berg et al. (2). A substantial increase in performance was achieved in the last five years by introducing noteworthy, sequential improvements to previously developed methods. The procedure employing 2,3-dihydroxynaphthalene (DHN) and an oxidiser to enhance sensitivity, proposed in 2001 by Obata and van den Berg (3), was mainly pursued. Firstly, an increase in sample pH to 8.7 lead to a ~threefold decrease in the LOD (4): the same study demonstrated that this procedure does not require UV digestion prior to analysis at low organic matter concentrations, albeit an overnight acidification of the sample is necessary. In the following year, oxygen was introduced as a sensitivity enhancer for the detection of the Fe-(salycilaldoxime)$_2$ complex, presumably acting as a precursor for hydrogen peroxide (5), although the method was developed for speciation analysis and shows limited sensitivity. Dioxygen as a signal enhancer was subsequently applied to the methodology employing DHN as the complexing ligand and a small volume cell requiring 500 µL of sample only. The latter procedure achieved a LOD of 5 pM employing a deposition time of 30 s, reducing the overall analysis time to 8 minutes per sample (6).

Such a great improvement in detection capabilities and in the overall procedure was not paralleled by an understanding of the involved chemical processesse. Aim of the present communication is to underpin the mechanism responsible for such a high sensitivity and to establish a framework for the assessment of AdCSV procedures. These data will be employed to try and define alternative ligands or procedures which may provide better performances not only for total iron detection but also for the speciation procedure.

References: 1. J.H. Martin, Paleoceanography 5 (1990) 1-13. 2. C.M.G. van den Berg, Z.Q. Huang, J. Electroanal. Chem. 177 (1984) 269-280. 3. H. Obata, C.M.G. van den Berg, Anal. Chem. 73 (2001) 2522-2528. 4. L.M. Laglera, J. Santos-Echeandia, S. Caprara, D. Monticelli, Anal. Chem. 85 (2013) 2486-2492. 5. M.M. Abualhaija, C.M.G. van den Berg, Mar. Chem. 164 (2014) 60-74. 6. S. Caprara, L.M. Laglera, D. Monticelli, Anal. Chem. 87 (2015) 6357-6363.

Multiple Reaction Monitoring tandem mass spectrometry for the selective quantitative determination of Oxylipins in serum from n patients with systemic sclerosis

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Oxylipins are a new class of oxygenated metabolites of polyunsaturated fatty acids (PUFAs) that affect a broad range of physiological processes, including interestingly the initiation and signalling of the inflammatory response (1). The evident complexity of the cascade reactions triggered by inflammatory processes and the discovery of new oxylipin families with additional anti-inflammatory and pro-resolution effects has encourage researcher to set up analytical methods analysing a number of molecules as high as possible. Although the most of studies provide the isolation and analysis of single oxylipin species, only a limited number of analytical methods offer a comprehensive coverage of the oxylipin synthetic cascade applicable to a wide range of human biofluids. Nowadays, automatic rapid high performance liquid chromatography tandem mass spectrometry has become the technique of choice for several metabolite analysis thanks to the capacity to simultaneously separate and determinate multi component mixtures (2). Here, a method using liquid chromatography-electrospray tandem mass spectrometry (LC-MS/MS) in multiple reaction monitoring ion mode operating in negative ion mode has been developed for the determination of oxylipins pattern in serum from patients affected from systemic sclerosis. The simultaneous, sensitive, fast, and reproducible measurement of 80 oxylipins in a single MRM run might be useful in the clustering the pathology at different level of inflammation.

References n 1. Calder PC. Omega-3 Fatty Acids and Inflammatory Processes. Nutrients. 2010; 2: 355–374.

Reference n. 2. Astarita G, Kendall AC, Dennis EA, Nicolaou A. Targeted lipidomics strategies for oxygenated metabolites of polyunsaturated fatty acids. Biochim Biophys Acta. 2015;1851:456-468.

Quantitative analysis of catechins by Multiple Reaction Monitoring in tea, coffee and food supplements.

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Catechins are secondary metabolites of plants, The main role of phenolic compounds as metabolites in plants is food deterrence; because of their bitter taste they play a role in defense, but not only, in fact: they give mechanical support, attract pollinator insects, absorb harmful UV rays and are substances allelopathic.

The contribution of polyphenols to human diet varies enormously in relation to the type, quantity and quality of the consumed vegetables; The intake is generally considerable, just because they are the most antioxidant molecules represented in the vegetable kingdom. The main role of catechins in humans is to protect cells from damage caused by free radicals that develop with normal cell metabolism due to stress events (1).

The aim of the work was to develop a tandem mass spectrometry strategy in Multiple Reaction Monitoring to identify and quantify the catechins mainly contained in commonly used drinks such as tea and coffee and the subsequent application of the optimized method for dietary supplements analysis present on the market. Their content in these drinks is variable and depends on plant variety, growth conditions, long cultivation, harvesting methods and times, as well as conservation and machining processes (2).

Therefore, 75 species were selected to be monitored during a single LC MRM MS (5 minutes) analysis and for each compound the best two precursor ion-fragment ions transitions were selected (thanks to literature data) to ensure high selectivity and sensitivity to the analysis

The quantitative analysis was performed using the external standard method in a range of concentrations ranging from 0.1 to 25 pg/L.

Analytical parameters (e.g. LOD, LOQ, linearity, intraday ripetitivity...) were determined.

Reference n. 1. Ras, R.T.; Zock, P.; Draijer, R. Tea consumption enhances endothelial-dependent vasodilation; ameta-analysis. PLoS One 2011, 6(3).

References n. 2. Effect of Tea Theaflavins and Catechins on Microvascular Function, Fuchs, D.; de Graaf,Y.; Van Kerckhoven, R.; Draijer, R. Nutrients. 2014 Dec; 6(12): 5772–5785.

Volatile fraction analysis by HS-SPME/GC-MS and chemometric tools to characterize the flavor of *lager* craft beers

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Beer is one of the most popular and oldest alcoholic beverages in the world (1). In particular, *lager pilsner* is the category of low fermentation beers most common in continental Europe. In Italy, the production capacity of the breweries has increased along with the new ways of consumption: 13 million hectoliters of beer were produced in 2014, of which 3.3% of the production were handicrafts. Of course, this represents only a small part of the total but can already be considered surprising if one considers that in 2011 were only 1.1% (2).

Commercial beers are always microfiltrate and pasteurized while craft beers do not, and in fact the concept of artisanal beer among consumers is related to the highest quality beer. In Italy, however, the recent law does not mention the quality of the raw materials used, but defines only the production processes (3).

This study intends to characterize the two types of beer through the analysis of specific markers determined by studying the aromatic profile. The aromatic component of beer is very important, considering that aroma has a great influence on the consumer's acceptance and preferences of different products.

The headspace solid-phase microextraction (HS-SPME) technique followed by GC/MS analysis was performed to evaluate the volatile fraction of beer samples produced under different processes (handicraft methods or industrial processes). For headspace SPME was used a DVB/CAR/PDMS fiber who provided extraction of a wide range of volatile compounds with different polarities (4,5).

The monitoring of volatile fraction, which contributes to flavor definition, may represent an interesting tool to characterize beer samples in relation to the manufacturing processes.

Principal Component Analysis (PCA) was applied to experimental data set to identify volatile compounds, who confer a particular aroma, suitable to be used as potential quality/process markers in order to discriminate beer samples according to their production method. Hence, the proposed method may help to protect the craft beer from label frauds by verifying whether samples comply with statements concerning conditions set out by the law.

The preliminary outcomes are promising and the study assesses the possibility of differentiating and enhancing product types on the market at different prices, and providing process/product indicators as a tool to distinguish a beer also on aspects defined as "added values" that would justify the adoption of a "premium price" for craft beers.

References: 1. Berkhout, B., Bertling, L., Bleeker, Y., de Wit, W., Kruis, G., Stokkel, R., & Theuws, R. J., "The contribution made by beer to the European economy", Full report: December 2013. A report commissioned by The Brewers of Europe and conducted by Regioplan Policy Research and EY, 212; 2. Ravelli, G., Pedrini, M., "Rapporto 2015. Osservatorio ALTIS – UNIONBIRRAI sul segmento della birra artigianale in Italia". EDUCatt, Milano, 2015; 3. Art.35, DDL 1328-B, 2016; 4. Pinho O., Ferreira I., Santos L., "Method optimization by solid-phase microextraction in combination with gas chromatography with mass spectrometry for analysis of beer volatile fraction". Journal of Chromatography A, 1121, 2006, 145–153; 5. Moreira N., Meireles S., Brandão T., Guedes de Pinho P., "Optimization of the HS-SPME–GC–IT/MS method using a central composite design for volatile carbonyl compounds determination in beers". Talanta, 117, 2013, 523–531

Setup of new metrics in performance assessment and validation of NMR methods for fingerprinting and simultaneous multicomponent quantitative analysis

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The goal of this work was to set up validation procedures and new quality control parameters suitable for performance assessment in simultaneous multi component quantitative NMR analysis and NMR fingerprinting methods. In order to achieve the goal, three inter-laboratory comparisons (ILCs) were organized. The first one(1,2) consisted in the analysis of wheat and flours aqueous extracts (4 samples) and was aimed to ascertain the statistical equivalence of the scaled NMR spectra. 780 NMR spectra were produced by 32 participants using 39 different NMR spectrometers. Seven signals were submitted to univariate internationally agreed statistics typically applied in performance assessment of ILC participants.The second ILC(3) regarded a model mixture made up of five compounds. In particular, a model mixture made up of five compounds [Aldicarb, Methamidophos, Oxadixyl, Pirimicarb and 3-(trimethylsilyl)-2,2,3,3-tetradeutero-propionic acid sodium salt (TSP)] dissolved in deuterated water was submitted to NMR analyses. 1260 NMR spectra were produced by 30 participants using 34 different NMR spectrometers. The analytical target of the second ILC was the quantification of analytes by the calibration line method. Such a method was chosen as it allows for identification of a theoretical line to be taken as reference in performance assessment. The third ILC consisted in the analysis of wine grape juice (7 samples) and was aimed to confirm the statistical equivalence of the scaled NMR spectra and to quantify several metabolites by standard addition method. 2310 NMR spectra were produced by 54 participants using 66 different NMR spectrometers. Results show that quantitative NMR is a robust quantification tool. Performance assessment was carried out on single component quantification, by the popular and traditional z-score, and on multi-component analyses by means of a new performance index (named Q_p-score) which is related to the difference between the experimental and the consensus values of the slope of the calibration lines. By an analogous reasoning followed for z-score, performance assessment by Q_p-score is considered satisfactory when $|Q_p|\leq 2.0$, questionable when $2.0<|Q_p|<3.0$ and unsatisfactory when $|Q_p|\geq 3.0$. Qp-score is a parameter suitable for harmonization of fingerprinting protocols and simultaneous quantitative multi component analysis. Such parameter, that was designed considering consolidated internationally agreed statistics, represents an unbiased evaluation tools for NMR method validations.

References
1. "Validation of a 1D 1H-NOESY experiment for fingerprinting of wheat and flour". V. Gallo, N. Intini, P. Mastrorilli, M. Latronico, P. Scapicchio, A. Rizzuti et al. "NMR Inter-Laboratory Comparisons" Series, Vol. 1 (Sept 2015). ISBN: 97888999259112 –Ed. NeP Edizioni, Rome
2. "Validation of NMR fingerprinting methods: effects of processing on measure reproducibility and laboratory performance assessment". V. Gallo, N. Intini, P. Mastrorilli, M. Latronico, P. Scapicchio, A. Rizzuti, S. Todisco et al. "NMR Inter-Laboratory Comparisons" Series, Vol. 2 (Sept 2016). ISBN: 9788899259709 – Ed. NeP Edizioni, Rome
3. "Performance assessment in fingerprinting and multi component quantitative NMR analyses". V. Gallo, N. Intini, P. Mastrorilli, M. Latronico, P. Scapicchio, A. Rizzuti, Analytical Chemistry, 87 (2015), 6709–6717.

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The oxidative potential of $PM_{2.5}$ and PM_{10} at an urban site in Lecce: influence of the sources of combustion and transport of Saharan dust

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Atmospheric particulate matter (PM) has adverse effects on human health (1). Although the PM's toxic effect on human health can be related to its chemical-physical properties, toxicity mechanisms are not yet fully known. Related studies suggested that reactive oxygen species (ROS) either transported on particles or catalytically generated by particles through red-ox reactions can be important sources of cellular damages. For this reason, in the international scientific community, the oxidative potential (OP) of atmospheric particulate matter is considered a practical indicator to investigate potential risks for specific human health problems.

Contribution to the oxidative potential of specific anthropogenic sources, such as road traffic, biomass combustion and industrial emissions, has been studied at several observation sites. However, at the present information regarding the OP of natural source are still insufficient. As for example, data related to the contribution of the Saharans dust (Saharan Dust Outbreak, SDO) on the oxidative potential are not yet available.

The aim of this work was to fill this gap by evaluating the OP of water-soluble $PM_{2.5}$ and PM_{10} samples taken at the Environmental-Climate Observatory of Lecce (Southern Italy, 40°20’8’’N-18°07’28’’E, 37 m asl), regional station of the Global Atmosphere Watch (GAW) network, by using the a-cellular DTT (dithiothreitol) assay (2). The OP values of three groups of samples were compared: standard having concentrations and carbon content similar to the yearly averages values; high carbon samples associated to combustion sources (mainly road traffic and biomass burning) and Saharan dust outbreaks (SDO). DTT activity normalised by volume (DTT_V), representative of personal exposure, and normalised by mass (DTT_M), representing source-specific characteristics, were investigated. The DTT_V is an extensive property that increases with the increase of PM concentration, well correlated with secondary organic carbon concentration. It is significantly larger in fine particles $PM_{2.5}$ with respect to coarse fraction $PM_{2.5\text{-}10}$. DTT_V is larger for high carbon content samples but during SDO events is statistically comparable with that of standard samples. DTT_M is larger on $PM_{2.5}$ with respect to PM_{10} and the relative differences between the two size fractions is maximised during SDO events. This indicate that Saharan dust advection is a natural source of particles having a lower specific OP with respect to the other sources acting on the area. Results suggest that OP could be an useful quantitative indicator to be used in epidemiological studies, in addition to PM mass concentrations, in regions frequently affected by high pollution events due to Saharan dust advection.

1. Pope, C.A.,. Ezzati M, Dockery, D.W.(2009). N. Engl. J. Med. 360, 376-386.
2. Chirizzi D., Cesari D., Guascito M.R., Dinoi A., Giotta L., Donateo A., Contini D. (2017). Atmospheric Environment (in press), 10.1016/j.atmosenv.2017.05.021.

Synthesis, characterization and electrochemical activity of α-MoO_3/Pt modified electrode to methanol oxidation

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The MoO_3 nanostructures have been synthesized by various methods, including pulsed laser deposition, thermal evaporation, RF magnetron sputtering sol–gel, hydrothermal, spray pyrolysis, chemical vapour deposition, mechanical exfoliation, molecular beam epitaxy and electrodeposition. These research works have revealed that MoO_3 exists as one of three polymorphic forms: a thermodynamically stable orthorhombic phase, a metastable monoclinic phase and a metastable hexagonal-phase. Many reports suggest that the majority of the MoO_3 materials are in the orthorhombic phase, the monoclinic phase or their mixtures (1,2).

In this communication we reported the synthesis of MoO_3 microplates by thermally oxidizing molybdenum foils at ambient atmosphere through resistive heating with no participation of templates or catalysts. Grown microplates MoO_3 structures were characterized by using scanning electron microscopy (SEM), transmission electron microscopy (TEM) coupled with selected area diffraction pattern (SAD), X-ray powder diffraction (XRD), micro-Raman and photoluminescence (PL) spectroscopy. The MoO_3 microplates synthesized after 60 min resistive heating, that have orthorhombic single-crystalline structures grown preferentially along the [001] direction. They are about 100-200nm in thickness and a few tens micrometers in length. As heating time proceeds to 80 min, plates of α-MoO_3 form a branched structure. A more attentive look shows that a primary plates formed at until 60 min could serve as substrates for the subsequent growth of secondary belts.

The electrocatalytic activity of α-MoO_3 plates on Pt electrodes was carried out by Cyclic Voltammetry (CV) in neutral phosphate buffer to investigate the electrochemical properties of α-MoO_3/Pt modified electrode against methanol oxidation. Electrochemical characterization of MoO_3 hierarchical structures highlighted the involvement of Mo(IV)/Mo(VI) species in electrodic processes at neutral pH, being diffusion controlled in oxidation and surface controlled in reduction. Moreover, the results obtained for electrochemical oxidation of methanol by Pt electrodes modified with MoO_3 structures showed the enhanced catalytic properties of Pt when acting in synergy with MoO_3 plate structures (3).

References:
1. Martínez, H., Torres, J., Rodríguez-García, M., & Carreño, L. L. (2012). Physica B: Condensed Matter, 407(16), 3199-3202.
2. Lu, X., Wang, R., Yang, F., Jiao, W., Liu, W., Hao, L., & He, X. (2016). Journal of Materials Chemistry C, 4(28), 6720-6726.
3. E. Filippo, F. Baldassarre, M. Tepore, M. R. Guascito, D. Chirizzi and A. Tepore.. Nanotechnology 28 (2017) 215601 (12pp). https://doi.org/10.1088/1361-6528/aa67c9

Model of the electrical response of anti-thrombin TBA aptamer in bio-sensing applications

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Medicine is recently focusing on DNA-based treatments to improve prevention, personalized therapies and to achieve a less invasive and early diagnosis. Accordingly, researchers are devoted to design and produce a novel kind of macromolecules, the aptamers, single-stranded DNA and RNA sequences artificially produced to bind, with high affinity, the assigned ligands. Their mechanism of ligand binding is quite similar to the recognition process used by monoclonal antibodies, finding applications in therapies covering illnesses from cancer to cardiovascular diseases. Among aptamers, the DNA 15-mer TBA is one of the best known, both in structure and function. Its therapeutic action, related to the ability of binding the exosite II of thrombin, produce an effective inhibition of platelet thrombus formation. High affinity with thrombin has selected this aptamer as the ultimate component of thrombin sensors. In particular, Cai (1) proposed a TBA-based label-free sensor, able to detect thrombin with high selectivity and sensitivity by using the Electrochemical Impedance Spectroscopy technique with an electrode TBA functionalized. A sensitive change (up to about 200%) in the electrochemical impedance upon enzyme–aptamer complex formation was revealed. Some other data concerning structure and function of TBA came from X-ray spectroscopy (2). In particular, the structure of the aptamer-enzyme complex has been resolved in the presence of K+ and Na+. The different effects in thrombin inhibition due to the presence of these ions seem to be related to subtle differences in the aptamer-thrombin complex (2).

In this contribution we use the theoretical approach known as proteotronics (3) to set up a microscopic model of the electrical response of TBA alone and complexed with thrombin. The macromolecule is mapped into a network, by using an all-nucleobase/amino acid coarse grained procedure. Each node of the network corresponds to a single nucleobase/amino acid and contains three main data: the position of the C1 atom (C□), the resistivity and the polarizability. Two nodes are connected only if their physical distance is smaller than an assigned cut-off radius, RC. Each link mimics an elementary electrical impedance, that in this case, is an RC parallel circuit, in agreement with the experimental results. TBA has been analyzed in 3 different configurations: a. native state, b. complex state with K+ or Na+ c. active state. The calculated electrical resistance of the network describing the native structure of TBA is compared with those of the networks of the complex in the presence of both K+ and Na+. The complex shows a relevant improvement of resistance with respect the TBA alone, as observed in experiments, particularly in the presence of K+. This result nominates resistance measurement as a novel test of aptamer-ligand affinity. The capture of thrombin produces a change of TBA free energy which is described as a change of the interaction radius, RC, used for building the network. Finally, by analyzing the mechanism of TBA-thrombin conjugation and considering that dose-response observed in experiments depends on the fraction of TBAs which capture the thrombin, we are able to reproduce the experimental data and the agreement is quite good.

References:

1. Cai et al. 2006. Sensors Actuators B 114 433–7; 2. Russo-Krauss 2012. Nucleic acids research, gks512; 3. Alfinito et al. 2015. FL:CRC Press. 4. Alfinito et al. 2017. Nanotechnology 28(6):065502.

Smartphone-based cell biosensors: a new tool for rapid on-site detection of chemical agents

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The routine monitoring of water, food, and the environment for chemical and biological threat agents is hampered by the fact that available techniques usually require clean samples and sophisticated equipment. Alternatively, unconventional analytical tools that allow rapid and low-cost monitoring of complex matrices are provided by biosensors. In particular, cell biosensors present the important feature of assessing the biological effects of a target analyte and its bioavailability. All chemical and biological threat agents share the ability to interact with molecular targets (e.g., receptors, membranes..) and therefore cells can be employed as "living sentinels". In the frame of the project "Cell biosensors for detection of chemical and biological threats", funded by NATO-SPS, we developed a battery of bioengineered cell biosensors "tailored" to respond to different agents by the generation of measurable and quantitative dose-dependent bioluminescent signals. As first proof-of-concept, *S. cerevisiae* yeast cells were bioengineered to respond to toxicants and endocrine disrupting chemicals acting via estrogen/androgen receptors. The bioengineered cells were integrated into 3D printed ready-to-use cartridges and low-cost smartphone adaptors were created using a desktop 3D printer to provide a mini-darkbox. Preliminary results will be presented about analytical performance of the smartphone-based device and its suitability for on-site surveillance.

Soil's fingerprinting for forensic applications: GC-MS as an useful tool

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The unique identification of soils is mandatory in several forensic investigations, as in the case of land under shoes of a murder victim to match the soil at the crime scene.

Different approaches have been proposed up to now to investigate this problem: among them, microscopic techniques, genome study of the bacterial flora in the soils, and chemical techniques that mostly rely on the determination of trace elements in the samples, usually by ICP or neutron activation analysis. In this study, different soils have been characterized for the volatile and semi-volatile organics. To this purpose, forest lands, farmlands, burnt ground, urban borders and grass, have been collected, characterized in terms of N content, COD, TOC, dry residue at 550°C, pH, etc, and analyzed by GC-MS. Different sample treatments have been considered to find organics that could be identified as fingerprint of a specific soil, from the headspace analysis to the solvent extraction prior and after pyrolysis of the soil (at 200°C), to the analysis of sugars, organic acids and similar compounds after derivatization of the soil extract with N,O-Bis(trimethylsilyl)trifluoroacetamide/trimethychlorosilane (1).The organics identified (polycyclic hydrocarbons, pesticides, sugars and terpenic compounds) are evaluated with the aim to assign some of them, whenever possible, to a certain typology of soil.

References: 1. Derivatization of carbohydrates for GC and GC–MS analyses A.I. Ruiz-Matute, O. Hernández-Hernández , S. Rodríguez-Sánchez , M.L. Sanz , I. Martínez-Castro. Journal of Chromatography B, 879 (2011) 1226–1240

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Cinti Stefano	ANA/ELE/GS-KN01
Cinti Stefano*	ANA-OR38
Cioffi Lorenzo	ANA-PO51 ANA-OR03
Cioffi Nicola	ANA-OR44 ANA-OR46
	ANA-PO120
Cioffi Nicola*	ANA-KN09
Cioffi Nicola*	ANA-PO89
Ciotoli Eleonora	ANA-PO109
Ciriello Rosanna	ANA-PO07
Clemente Maurizio	ANA-OR44
Cocco Federica	ABC/ANA/FIS-OR09
Cocco Federica*	ANA-PO02
Codée Jeroen D.C.	ANA/MAS-OR01
Colizza Ester	ABC/ANA-OR04
Colombaioni Laura	ANA-PO41
Colombi Cristina	ANA-OR33
Colombini Maria Perla	ABC/ANA/FIS-OR10
Colozza Noemi*	ANA-OR08
Compagnone Dario	ANA/MAS-OR03
	ANA-PO16
	ANA-PO60
	ANA-PO80
Conca Eleonora	ANA/ELE/GS-OR03
	ANA-PO17
	ANA-PO108
	ANA-PO27
Conca Eleonora*	ANA-OR09
Consolandi Clarissa	ANA-PO68
Consolo Mariella	ANA-PO132
Contado Catia	ANA-PO45

Contado Catia*	ANA-OR24
Conte Amalia	ANA-OR44
Conte Eleonora	ABC/ANA/FIS-OR07
	ANA-PO70
	ANA-PO71
Contini Daniele	ANA-PO136
Contini Matteo	ANA-OR32
Contursi Michela	ANA-OR39
	ANA-PO90
Corbella Lorenza	ANA-OR33
Cordoni Davide	ANA-PO16
Corradini Claudio	ANA-PO76
	ANA-PO86
Corradini Danilo*	ANA-PO46
Corradini Roberto	ANA-PO92
Corricelli Michela	ANA-OR36
Cortese Claudio	ANA-OR38
Costa Bassetto Victor	ANA/ELE/GS-KN02
Costamagna Giulia*	ANA-PO13
Costantini Monica	ANA-PO93
	ANA-PO94
Cotellese Roberto	ANA-PO49
Covelli Stefano	ANA-PO08
Coviello Donatella*	ANA-PO90
Coviello Donatella*	ANA-OR39
Cozzi Giulio	ANA-PO14
Crea Francesco	ANA-OR16
	ANA-PO32
Crescenzi Carlo	ANA-PO42
	ANA-PO56
	ANA-OR26
Crescenzi Carlo*	ANA-OR22
Criste Cecilia	ANA-PO96
Critto Andrea	ABC/ANA-KN01
Croce Sara	ANA-PO08
Crosera Matteo	ANA-PO01
	ANA-PO08
Crosera Matteo*	ANA-OR06
Cucca Lucia	ANA-PO140
Cuccia Eleonora	ANA-OR33
Cucciniello Raffaele	ABC/ANA-KN03
	ABC/ANA-OR07
	ANA-PO18
Cuomo Francesca	ANA-PO44

Curci Alessandra	ANA-PO89
Curini Roberta	ANA-OR07
	ANA-PO127
D’Acapito Francesco	ANA-PO95
D´Alessio Pasquale	ANA-PO131
D’Archivio Angelo Antonio*	ANA-PO114
D’Ulivo Alessandro	ANA-PO112
Dalcanale Enrico	ANA-PO92
Dale Nicholas	ANA/ELE/GS-OR02
Dall’Aglio Lorenza	ABC/ANA-OR07
Dall’Ara Alice	ANA-PO112
Dalle Carbonare Luca	ANA-PO70
Dallo Federico*	ANA-PO14
Damiano Fabrizio	ANA-PO68
D'Andrea Luca Domenico	ANA-OR17
Daniele Salvatore	ANA-PO119
D'Annibale Andrea	ANA-PO91
D'Archivio Angelo Antonio*	ANA-PO15
De Bellis Gianluca	ANA-PO68
De Benedetto Giuseppe Egidio*	ANA-PO68
De Benedetto Giuseppe Egidio*	ABC/ANA/FIS-OR08
De Benedetto Giuseppe Egidio*	ANA-PO03
De Cesare Giampiero	ANA-PO98
	ANA-PO107
De Gara Laura	ANA-PO46
D’Elia Marcello	ANA-PO139
De Laurentiis Francesco	ANA-PO124
De Luca Antonio	ANA-PO102
De Luca Domenico A.	ANA-PO20
De Luca Maria	ANA-PO97
De Luca Silvia	ANA-PO109
De Maria Letizia	ANA-OR43
De Nunzio Giorgio	ANA-PO138
De Petris Giulia	ANA/MAS-OR06
De Rosa Lucia	ANA-OR17
De Rosa Margherita	ANA-PO11
De Stefano Concetta	ANA-OR16
	ANA-PO32
	ANA-PO33
	ANA-PO34
	ANA-PO84
De Tommaso Gaetano*	ANA-OR17

	ANA-PO120
Innocenti Massimo*	ANA-OR46
Intini Nicola	ANA-PO135
Irto Anna	ANA-OR16
Irto Anna*	ANA-PO32
Isca Clelia	ABC/ANA/FIS-OR06
Isernia Carla	ANA-OR17
Ismail Omar H.	ANA-OR12
	ANA-PO47
Isse Abdirisak Ahmed	ANA-OR19
Iuliano Mauro	ANA-OR17
Iurlo Matteo	ANA/ELE/GS-OR05
Izzi Margherita	ANA-OR44
Izzo Simona	ANA-PO110
Janssens Koen	ABC/ANA/FIS-KN01
Kano Kenji	ANA-PO82
	ANA-PO83
Koehler Brigit	ABC/ANA-KN02
Koivula Anu	ANA-OR40
Kornejew Eckhart	ANA-PO91
Kranz Christine	ANA-KN09
La Barbera Giorgia	ANA-PO43
	ANA-PO48
La Barbera Giorgia*	ANA-OR02
La Bianca Mariacristina	ANA-OR19
La Nasa Jacopo	ABC/ANA/FIS-KN02
Lachowicz Joanna Izabela*	ANA-PO33
Laganà Aldo	ANA-OR11
	ANA-OR42
	ANA-PO43
	ANA-PO48
	ANA-PO66
Landelius Tomas	ABC/ANA-KN02
Lando Gabriele	ANA-OR16
	ANA-PO84
Lando Gabriele*	ANA-PO34
Langerame Fausto	ANA-PO07
Langley John	ANA-PO04
Lannuzel Delphine	ANA-PO09
Lasagna Manuela	ANA-PO20
Latronico Mario	ANA-PO135
Latruwe Kris	ANA-KN07
Lavacchi Alessandro	ANA-PO95

Leech Donal	ANA-OR20
Legrand Stjin	ABC/ANA/FIS-KN01
Lesch Andreas*	ANA/ELE/GS-KN02
Lesch Andreas	ANA-PO113
Li Donghao	ANA-PO57
	ANA-PO58
Li Qianjin	ANA-PO42
Licandro Emanuela	ANA-OR19
	ANA-PO81
	ANA-PO99
Lisdat Fred	ANA-PO91
Lista Florigio	ANA/ELE/GS-OR07
Lo Re Alessandra	ABC/ANA-OR02
Lo Sterzo Claudio	ANA-PO60
Lomonaco Tommaso	ANA-PO38
	ANA-PO63
	ANA-PO100
Lopez Francesco	ANA-PO44
López-Lorente Ángela I.	ANA-KN09
Lopreside Antonia	ANA-PO88
Lopreside Antonia*	ANA-PO139
Losito Ilario*	ANA-OR21
Losito Ilario	ANA-PO75
Lucarelli Franco	ANA-KN03
	ANA-OR34
Łucejko Jeannette Jacqueline	ABC/ANA/FIS-OR10
Lucentini Luca	ANA-KN01
Ludwig Roland	ANA-OR40
Lupi Angelo	ANA-OR34
	ABC/ANA-OR05
Ma Biao	ANA-PO58
Macii Francesca	ANA-PO39
Maggi Maria Anna	ANA-PO15
	ANA-PO114
Magi Emanuele	ANA-OR29
Magi Emanuele*	ANA-PO77
Magnacca Giuliana	ANA-PO20
Magnani Luca	ANA-OR05
Magrì Andrea	ANA-OR47
	ANA-PO109
Maietti Annalisa	ANA-OR04
Maitane Olivares	ABC/ANA/FIS-KN02
Malacaria Luana	ANA-OR14

Malacrida Claudia	ANA-PO99
Malandrino Mery	ANA-PO27
	ANA/ELE/GS-OR03
	ANA-OR09
	ABC/ANA-OR05
	ANA-PO17
	ANA-PO108
	ABC/ANA-OR01
Malaspina Fabrizio	ANA-PO129
Malavasi Lorenzo	ANA-OR32
	ANA-PO36
Malegori Cristina	ANA-PO05
	ANA-PO118
	ANA-PO119
Malegori Cristina*	ANA-OR48
Malgieri Gaetano	ANA-OR17
Malitesta Cosimino	ABC/ANA-KN03
	ANA-PO18
	ANA-PO42
	ANA-PO97
Mancini Ignazio M.	ANA-OR30
Manera Maria Grazia	ANA-OR23
Manfra Michele	ANA-PO55
	ANA-PO62
Manfredi Carla *	ANA-PO35
Manfredi Marcello*	ANA-PO70
Manfredi Marcello*	ANA-PO71
Manfredi Marcello	ABC/ANA/FIS-OR07
	ANA-OR25
	ANA-OR49
	ANA-PO10
	ANA-PO19
	ANA-PO20
	ANA-PO23
	ANA-PO24
	ANA-PO121
	ANA-PO122
Manfredi Marcello*	ANA-OR05
Mangiacotti Michele	ANA-PO52
Manicardi Alex	ANA-PO92
Manniello Michele Dario	ANA-OR26
Mantini Caterina	ANA-PO27
Maraschi Federica	ANA-OR32

	ANA-PO37
Marassi Valentina*	ANA-OR13
Marcaccio Massimo	ANA/ELE/GS-OR05
	ANA-OR20
Marchesani Giuliana*	ANA-PO52
Marchetti Alessia	ANA-PO79
Marchetti Nicola*	ANA-OR04
Marchetti Simone	ANA-OR18
Marchetti Simone*	ANA-OR43
Marchiandi Sergio	ANA-PO105
Marcomini Antonio*	ABC/ANA-KN01
Marengo Emilio	ANA-OR05
	ABC/ANA/FIS-OR07
	ANA-OR25
	ANA-OR49
	ANA-PO10
	ANA-PO19
	ANA-PO20
	ANA-PO23
	ANA-PO70
	ANA-PO71
	ANA-PO121
	ANA-PO122
Margiotta Nicola	ANA-PO89
Mariani Federica	ANA/ELE/GS-OR01
Mariani Stefano	ANA-PO97
Marinelli Tecla	ANA-OR30
Marini Federico	ANA-OR47
	ANA-PO29
	ANA-PO109
	ANA-PO110
	ANA-PO111
	ANA-PO115
Marletti Matteo	ABC/ANA-OR01
Marrazza Giovanna*	ANA-PO96
Marrazza Giovanna*	ANA-PO22
Martellini Tania	ANA-PO22
Marti Matteo	ANA-OR07
Martinelli Nicola	ANA-PO71
Martyna Agnieszka	ANA-PO128
Marzani Luca	ANA-PO22
Marzilli Mario	ANA-PO38
Marzio Rosi	ANA/MAS-OR06

Mascherpa Marco Carlo	ANA-PO112
Mascini Marcello	ANA-PO80
Masi Salvatore	ANA-OR30
Massi Alessandro	ANA-PO85
Massoud Renato	ANA/ELE/GS-KN01
	ANA-OR38
Mastrangelo Rosangela	ABC/ANA/FIS-OR03
Mastrocinque Raffaella	ANA-PO62
Mastrorilli Piero	ANA-PO135
Mastrorocco Antonella	ANA/MAS-KN01
Materazzi Stefano	ANA-PO125
	ANA-PO126
	ANA-PO69
Mattarozzi Monica	ANA-PO67
	ANA-PO92
	ANA-PO93
	ANA-PO94
Mattonai Marco	ANA-PO79
MattorreBenedetta	ANA-PO68
Mauro Marcella	ANA-OR06
Mayer Alice	ANA-PO24
Mazza Maria	ANA-OR05
Mazzaracchio Vincenzo*	ANA/ELE/GS-OR07
Mazzei Franco	ANA-OR20
	ANA-OR40
	ANA-PO91
Mazzeo Rocco*	ABC/ANA/FIS-KN01
Mazzeo Rocco	ANA-PO05
Mazzola Mauro	ANA-OR34
	ABC/ANA-OR05
Mazzone Giuseppina	ANA-OR30
Mazzotta Elisabetta*	ANA-PO97
Mazzotta Lorenzo	ANA-PO03
Mazzuca Claudia	ANA-PO117
Mazzucco Eleonora	ANA-PO71
	ANA-PO122
Mazzucco Eleonora*	ANA-PO23
Mazzucco Eleonora*	ANA-PO24
Meier Florian	ANA-PO45
Melfi Maria Teresa*	ANA-PO53
Meloni Daniela	ANA-KN03
Melucci Dora	ANA-PO124
Mentana Annalisa	ANA-PO53

	ANA-PO57
	ANA-PO58
	ANA-PO78
Mercogliano Paola	ABC/ANA-KN01
Merli Daniele*	ANA-PO140
Merli Daniele	ANA-OR43
Merlo Francesca	ANA-OR32
Mezgec Karin	ABC/ANA-OR04
Micheli Laura*	ANA-PO117
Micheli Laura	ANA-PO21
Michelini Elisa	ANA-PO88
	ANA-PO139
Mihali Voichita	ANA-OR19
Milanese Chiara	ANA-PO36
Milano Francesco	ANA-PO138
Milea Demetrio	ANA-OR16
Milica Jovic	ANA/ELE/GS-KN02
Minella Marco	ABC/ANA-OR02
	ABC/ANA-KN02
Minella Marco*	ANA-OR45
Minero Claudio	ABC/ANA-KN02
	ANA-OR45
Miniotti Eleonora	ANA-PO24
Minunni Maria	ANA-OR23
	ANA-PO103
	ANA-PO104
Mirabile Antonio	ABC/ANA/FIS-OR02
	ANA-PO06
Mirasole Cristiana	ANA-OR29
Mirasoli Mara*	ANA-PO98
Mirasoli Mara	ANA-KN02
	ANA-OR37
	ANA-PO113
	ANA-PO85
	ANA-PO106
Mirasoli Mara	ANA-PO107
Mistri Michele	ANA-PO12
Mizaikoff Boris	ANA-KN09
Močnik Grisa	ABC/ANA-OR07
Modugno Francesca	ABC/ANA/FIS-OR10
Mondello Luigi	ANA/MAS-KN02
	ANA-KN04
Montalbano Letizia	ABC/ANA/FIS-OR02

Montegrossi Giordano	ANA-PO95
Montesano Camilla	ANA-OR07
	ANA-PO16
	ANA-PO127
Monticelli Damiano*	ANA-PO130
Montis Costanza	ABC/ANA/FIS-OR03
Montone Carmela Maria	ANA-OR42
	ANA-PO48
	ANA-PO66
Montone Carmela Maria*	ANA-OR11
Montoya Noemì	ABC/ANA/FIS-OR05
Mora Paolo	ANA-PO67
Moretti Sacha	ANA-OR27
Moro Isabella	ANA-PO40
Moroni Beatrice	ABC/ANA-OR05
Moscone Daniela	ANA/ELE/GS-OR07
	ANA/ELE/GS-KN01
	ANA/ELE/GS-OR06
	ANA-OR08
	ANA-OR38
Motta Oriana	ABC/ANA-OR07
Mussini Patrizia Romana*	ANA-PO99
Mussini Patrizia Romana	ANA-PO81
Mussini Patrizia Romana*	ANA-OR19
Naccarato Attilio	ANA-PO74
Naccarato Attilio*	ANA-OR27
Napoli Anna	ANA-PO30
Nardiello Donatella	ANA-PO53
	ANA-PO57
	ANA-PO58
	ANA-PO78
Nascetti Augusto	ANA-PO98
	ANA-PO107
Natale Anna	ANA-PO53
	ANA-PO78
Natale Gabriella	ANA-OR19
	ANA-PO99
Natile Giovanni	ANA-PO89
Nava Silvia	ANA-KN03
Navarra Gabriele	ABC/ANA/FIS-OR09
Naviglio Daniele*	ANA-PO54
Naviglio Daniele*	ANA-PO72
Naviglio Daniele	ANA-PO59

Neagu Daniela	ANA/ELE/GS-OR06
	ANA/ELE/GS-OR07
Neri Placido	ANA-PO11
Netti Paolo Antonio	ANA-PO59
Nicolardi Simone*	ANA/MAS-OR01
Nicoletti Isabella	ANA-PO46
Nicolis Stefania	ANA-PO37
Nisi Stefano	ANA-PO114
Notardonato Ivan*	ANA-OR28
Notardonato Ivan*	ANA-PO25
Novellino Ettore	ANA-PO62
Nurchi Valeria Marina	ANA-PO33
Olivares Maitane	ABC/ANA/FIS-KN02
Oliveri Paolo	ANA-OR48
	ABC/ANA/FIS-KN01
	ANA-PO118
	ANA-PO119
Oliveri Paolo*	ANA-PO05
Olivieri Oliviero	ANA-PO71
Onida Barbara	ABC/ANA-OR02
Onor Massimo	ANA-PO41
	ANA-PO112
Onor Massimo*	ANA-PO100
Orbelli Biroli Alessio	ANA-PO99
Orlandi Marco*	ABC/ANA/FIS-OR10
Orlandini Serena	ANA-OR03
	ANA-PO50
	ANA-PO51
	ANA-PO116
Orlando Ilaria	ANA-PO89
Ornaghi Paola	ANA-PO86
Orsini Francesca	ANA-PO46
Ortiz Maria Cruz	ANA-PO116
Ostacolo Carmine	ANA-PO55
	ANA-PO62
Östmana Conny	ANA-OR26
Pace Giandomenico	ANA-KN03
Pacifici Laura	ANA-PO129
Paciulli Maria	ANA-PO86
Padoan Sara*	ABC/ANA-OR03
Pagano Francesco*	ANA-PO55
Pagano Francesco	ANA-PO62
Palazzo Gerardo	ANA-KN09

Severi Mirko*	ABC/ANA-OR04
Sferlazzo Damiano Massimiliano	ANA-KN03
Shinde Sudhirkumar	ANA-PO42
Siciliano Maria	ABC/ANA-KN03
	ANA-PO18
Siciliano Tiziana	ABC/ANA-KN03
	ANA-PO18
Siculella Luisa	ANA-PO68
Silvestri Simone	ANA-PO23
	ANA-PO24
Simeoni Maria Chiara	ANA-PO60
Simoni Patrizia	ANA-OR37
Sogne Vanessa	ANA-PO45
Soldà Alice	ANA/ELE/GS-OR05
Soldà Alice*	ANA/ELE/GS-OR02
Sommella Eduardo	ANA-PO55
	ANA-PO62
Soriente Annunziata	ANA-PO11
Sorrentino Fiodor	ANA-PO100
Spadaccino Giuseppina	ANA-PO53
	ANA-PO57
	ANA-PO58
	ANA-PO78
Speltini Andrea*	ANA-OR32
Speltini Andrea*	ANA-PO36
Speltini Andrea*	ANA-PO37
Sportelli Maria Chiara	ANA-KN09
Sportelli Maria Chiara*	ANA-OR44
Sprovieri Francesca	ANA-OR27
Stenni Barbara	ABC/ANA-OR04
Stevanin Claudia	ANA-PO12
Stevar Daniela A.	ANA-OR40
Stjin Legrand	ABC/ANA/FIS-KN01
Strafella Alessandra	ANA-PO112
Strambini Lucanos M.	ANA-PO97
Sturini Michela	ANA-OR32
	ANA-PO37
Tacchini Massimo	ANA-PO85
Tafur Marinos Janeth	ANA-PO13
	ANA-PO31
Tafur Marinos Janeth*	ABC/ANA-OR06
Tagarelli Antonio	ANA-OR14
	ANA-OR27

Tagarelli Antonio*	ANA-PO74
Takahama Satoshi	ANA-OR33
Talà Adelfia	ANA-PO68
Talotta Carmen	ANA-PO11
Tamburrini Diego	ABC/ANA/FIS-OR10
Tassone Antonella	ANA-OR27
Tempesti Paolo	ABC/ANA/FIS-OR03
Tepore Antonio	ANA-PO137
Tepore Marco	ANA-PO137
Termopoli Veronica*	ANA/MAS-OR05
Tessarolo Marta	ANA/ELE/GS-OR01
Testini Mariangela	ANA-PO68
Testolin Anna	ANA-OR36
Thomas Elizabeth R.	ABC/ANA-OR04
Thorsten Klein	ANA-PO45
Tinti Alessandro*	ANA-OR33
Tiraboschi Carla	ANA-OR31
Todisco Stefano	ANA-PO135
Togna Anna Rita	ANA-OR07
Tomassetti Mauro*	ANA-PO105
Tomassetti Mauro	ANA-PO110
Tomei Maria Rita*	ANA/ELE/GS-OR06
Tommasini Simone	ANA-PO123
Tonelli Domenica	ANA/ELE/GS-OR01
Torelli Paola*	ANA-PO134
Torresan Silvia	ABC/ANA-KN01
Torri Cristian	ANA-PO26
Torsi Luisa*	ANA-PL01
Tortolini Cristina	ANA-OR40
Tositti Laura	ANA-PO124
Trabace Maddalena	ABC/ANA/FIS-OR02
Tranvik Lars J.	ABC/ANA-KN02
Traversi Rita	ANA-KN03
	ABC/ANA-OR04
	ABC/ANA-OR05
Traversi Rita*	ANA-OR34
Tricase Angelo	ANA-KN09
Trifuoggi Marco	ANA-PO131
	ANA-PO132
Trinei Mirella	ANA/ELE/GS-OR05
Trivella Maria Giovanna	ANA-PO38
Troiani Anna	ANA/MAS-OR04
	ANA/MAS-OR06

Truzzi Cristina	ANA-PO27
Tumiati Simone	ANA-OR31
Ubaldi Paolo Giuseppe	ANA-OR05
Udisti Roberto	ANA-KN03
	ABC/ANA-OR04
	ANA-OR09
	ANA-OR34
Udisti Roberto*	ABC/ANA-OR05
Ungaro Fabrizio	ANA-PO123
Vaglio Sara	ANA-PO64
Valenti Giovanni*	ANA-PO113
Valenti Maria Teresa	ANA-PO70
Valentini Antonio	ANA-KN09
Vallée-Bélisle Alexis	ANA-KN08
	ANA-PO101
Valmacco Federico	ABC/ANA-OR01
Van der Burgt Yuri E.M.	ANA/MAS-OR01
Van der Werf Inez	ANA-PO06
Vanhaecke Frank	ANA-KN07
Vannutelli Gabriele*	ANA-PO127
Vannutelli Gabriele	ANA-OR07
Vardè Massimiliano	ANA-PO14
Vassura Ivano	ANA-PO26
Vecchione Raffaele	ANA-PO59
Venditti Francesco	ANA-PO44
Ventura Giovanni	ANA-PO65
Ventura Giovanni*	ANA-PO75
Venturini Elisa	ANA-PO26
Venzo Alfonso	ANA-OR15
Vincenti Flaminia	ANA-PO127
Vincenti Flaminia*	ANA-OR07
Vincenti Marco*	ANA-PO128
Vincenti Marco*	ANA-PO129
Vincenti Marco*	ANA-PO64
Viola Alessia	ANA-PO56
Vione Davide	ABC/ANA-OR02

	ABC/ANA-OR01
Vione Davide*	ABC/ANA-KN02
Vitale Vito	ANA-OR34
	ABC/ANA-OR05
Volino Sabato	ANA-PO35
Volpe Annalisa	ANA-OR44
Volpe Giulia	ANA/ELE/GS-OR04
	ANA-PO21
Volpi Giorgio	ANA-PO31
Volpin Stefano	ABC/ANA/FIS-OR06
Vovk Irena	ANA-PO46
Wei Ouyang	ABC/ANA-KN01
Wuhrer Manfred	ANA/MAS-OR01
Yiming Jia	ANA-PO05
Zadora Grzegorz	ANA-PO128
Zangheri Martina	ANA-OR37
	ANA-PO113
	ANA-PO98
Zangheri Martina*	ANA-PO106
Zangheri Martina*	ANA-PO107
Zangheri Martina*	ANA-KN02
Zangrando Roberta	ABC/ANA-OR03
Zanoni Robertino	ANA-PO91
Zappi Alessandro*	ANA-PO124
Zappi Daniele*	ANA-OR41
Zattoni Andrea	ANA-OR13
Zelano Vincenzo	ABC/ANA-OR06
	ANA-PO13
	ANA-PO31
Zenezini Chiozzi Riccardo	ANA-OR11
Zenezini Chiozzi Riccardo*	ANA-OR42
Zeni Luigi	ANA-OR18
Zerbetto Francesco	ANA/ELE/GS-OR05
Zirino Alberto	ABC/ANA-KN01
Zoia Luca	ABC/ANA/FIS-OR10
Zoroddu Maria Antonietta	ANA-PO33
Zou Yilin	ANA-PO57