Chimica dell’Ambiente e dei Beni Culturali

ABC-OR-01 Development and evaluation of new paint cross-section preparation procedures

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A polychrome sample is generally characterized by a multilayer (10-100 μm each) structure where both organic and inorganic compounds are present. The characterisation and spatial location of these substances is of the outmost importance both for technical studies and the evaluation of the state of conservation of the painting under examination. The characterization of the chemical composition of painting materials may be considerably limited by the way in which cross sections are prepared for analysis. In particular, when paint samples are embedded into synthetic resins (epoxy, polyester, acrylic) the characterisation of the organic components is hard to be achieved unambiguously. Furthermore, the cross section surface morphology can affect the analytical performances of FTIR microscopy applications when spectra are collected in both total reflection and ATR mode. Recently [1] KBr has been proposed as an alternative embedding system to avoid pollution from embedding resins. However, the proposed procedure has some drawbacks concerning the fact that KBr is highly hygroscopic and fragile. Moreover, the dry polishing technique adopted may result in the contamination of paint layers with materials belonging to other layers as well as the retention of KBr particles. The polishing procedure, when carried out not automatically, relies on the skill of the operator who plays a crucial role in obtaining flat and regular cross sections. In order to overcome such limitations NaCl is proposed as alternative embedding system. The obtained cross sections resulted to be harder and less hygroscopic. Moreover, KBr procedure has been improved in order to obtain more reproducible cross section. To this purpose KBr cross sections were further embedded in a resin support. The obtained block was then polished using a hand lap which allowed to better control the applied pressure.

Argon Ion Milling was also tested as an alternative polishing system to prevent intra layers and KBr pollution.

Standard and real samples were embedded following the above mentioned procedures and the preparation methods evaluated by confocal microscopy, SEM-EDX and FTIR microscopy in both total reflection and ATR mode.

[1] Prati S; .Joseph E; Sciutto G; Mazzeo R (2010) Acc. Chem. Res. 43: 792–801.

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ABC-OR-02 Application of scanning electrochemical microscopy as alternative immunochemical imaging technique for the detection of proteins in paint cross-sections

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The identification and localization of organic substances in paint complex stratigraphies plays a crucial role in studies on painting techniques and conservation of artworks. Immunological methods represent a valid approach for the detection of proteins in artistic samples thanks to the high specificity of antigen-antibody reactions, which would allow to distinguish between different proteins and to determine their biological source. Different detection procedures relying on specific labels can be applied for the recognition of immunocomplexes. Among them, chemiluminescence (CL) imaging already showed high performances in terms of spatial resolution and sensitivity, allowing the localization of proteins in paint cross-sections [1].

The present research has been focused on the development of an alternative detection approach for the immunolocalization of proteins (i.e., ovalbumin) in paint cross-sections based on Scanning ElectroChemical Microscopy (SECM) [2]. The immunochemical analysis has been performed directly on the paint cross-section using an anti-ovalbumin primary antibody and a secondary antibody labelled with horseradish peroxidase (HRP). The addition of a proper mediator has allowed the localization of the target protein by SECM through the detection of the products of the HRP-catalyzed oxidation reaction. Preliminary promising results have been obtained on cross-sections of samples from standard paint's mock ups.

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[2] G.Valenti, L.Bardini, D.Bonazzi, S.Rapino, M.Marcaccio, F.Paolucci, *J.Phys. Chem C,* 2010, *114* (50), 22165-22170.

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ABC-OR-03 Raman and luminescence spectroscopy of the "purple of the poor": the ancient colorant orcein

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Orcein is a natural dye widely used since ancient times for dyeing textiles but also for decorating miniatures and manuscripts. Known as the "purple of the poor", orcein was used in place of the more expensive Tyrian purple. Unlike the latter, orcein has a low lightfastness and in ancient works it is often faded. From a chemical point of view, orcein is a complex mixture of different colored compounds, they all share a common structure resulting from phenoxazone and a number of different substituents which are the various chromophores. In the present work, UV-Vis fluorescence combined with micro-Raman spectroscopy allowed for the non destructive identification of orcein in a fragment from the 9th century Bible de Théodulphe. Raman spectroscopy has been applied also for studying a parchment fragment sampled from a 16th century map of Auvergne. In both cases, subtracted shifted Raman spectroscopy (SSRS) has been exploited for removing the strong fluorescence background. Overall results have been confirmed by LC/MS Q-TOF analysis.

The electronic and vibrational characterization highlighted some interesting spectral differences with respect to a fresh orcein standard sample. Taking into account the poor lightfastness of the purple colorant, the same investigation has been carried out on artificially aged orcein, by exposure to visible light, reproducing the spectral modification observed on the ancient fragments.

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ABC-OR-04 Provenance and technological features of monochrome faiences recovered in Pompeii

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This study was carried out within the framework of a wider research project aimed at acquiring knowledge on technological processes, raw materials and decay phenomena of Roman finds (pottery, glass and mosaic)[1,2]. The research focuses on blue faiences recovered in Pompeii, most of whose remind the iconography, the decoration and the appearance typical of Egyptian faience[3,4]. The investigation was aimed at defining the compositional and structural features, to figure out provenance on the basis of their technological characteristics. Different complementary analytical techniques were used: SEM to investigate the morphological aspects of the samples and in particular the interfaces, μ-Raman Spectroscopy and XRPD to identify crystalline phases, and LA-ICP-MS to assess the elemental composition . Statistical data treatment of the elemental concentrations of bodies and glazes allowed to classify the objects into groups and to verify the previously established archaeological hypothesis suggesting an Egyptian provenance for faience of Pompeii. Also, analyses have permitted to identify raw materials, technology and to reconstruct the glazing method.

[1] van der Werf et al., *J. Archaeol. Sci.* 36, 2625 (2009)
[2] van der Werf et al., Proceed. of 4th Int. Congress on "Sci. and Tech. for the safeguard of Cul. Her. in the Med. Basin", vol. II, 300 (2010)
[3] Rossi. Vasi egizi invetriati importati in Italia (I sec a.C.-I sec d.C.). Mefra. 1994; 106, 319
[4] Di Gioia. La ceramica invetriata in area vesuviana (2006)

ABC-OR-05 FTIR and Micro-Raman characterization of ancient paper materials

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The archive and library assets are an important part of the national cultural heritage. In order to identify appropriate methods of preservation and restoration of such property, it is important to understand the current chemical-physical state of the artifact and how it can be influenced by the microstructure of the fibers that compose it. Since the nature of the aggregates forming the paper semi-crystalline polymers, the degree of crystallinity and orientation of the fibers have a significant influence on its mechanical properties. The native cellulose is mainly crystalline, with only a few amorphous areas, however, many physical and chemical reactions can lead to the increase of amorphous areas and to the susceptibility of a biological attack, as well as a greater fragility of the paper [1, 2].


Figure 1. Ancient Book.

Spectroscopy is one of the most powerful tools for the characterization of paper materials and the identification of the degradation products. This work describes the application of FTIR and Micro-Raman spectroscopy to the characterization of paper of high historical and artistic interest.

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ABC-OR-06 In-situ Laser-Induced Breakdown Spectroscopy (LIBS) and X-Ray Fluorescence (XRF) Analysis of Roman Silver Denarii

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This communication presents the results of a study performed on a large collection of silver roman republican denarii, encompassing about two centuries of history. The joint use of LIBS and XRF spectroscopy allowed for an accurate determination of the coins' elemental composition; the measurements, performed mostly in situ at the 'Monetiere' in Florence, revealed a striking correlation of the 'quality' of the silver alloy with some crucial contemporary events. This finding was used for classifying a group of denarii whose dating was otherwise impossible.

The comparison with other contemporary denarii allowed also to controvert a recent theory [1,2] on the origin of the so called 'serrated' denarii (denarii showing notched chisel marks on the edge of the coin).

Fig. 1 – One of the serrated denarii analyzed
(Gens Papia, Crawford 384/1)

[1] S. Balbi De Caro, G. Devoto, G.M. Ingo, T. De Caro, G. Chiozzini, *Bollettino di Numismatica*, 32-33 **1999**, 105 (in italian).

[2] G.M. Ingo, E. Angelini, T. De Caro, G.Bultrini, *Appl. Phys. A*, 79, **2004**, 171.

ABC-OR-07 Characterisation of synthetic varnishes and paint materials by analytical methods based on pyrolysis and mass spectrometry

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The wide use of synthetic polymers in art and in restoration makes mandatory the assessment of their stability and degradation pathways, and the development and evaluation of adequate analytical methods for their characterization.

This knowledge is extremely relevant for the selection of preventive conservation conditions as to reduce frequency and invasivity of restoration work.

In the context of the PAR-FAS Regione Toscana COPAC Project - *Preventive Conservation of Contemporary Art* (2011-2013) we applied two analytical methods based on pyrolysis and mass spectroscopy, namely direct exposure mass spectroscopy (DE-MS) and pyrolysis coupled with gas chromatography/ mass spectrometry (Py-GC/MS), to characterize a series of synthetic resins used as paint binders, varnishes and consolidants, before and after natural ageing (1-12 months): acrylic resins (Paraloid B67 and Acril 33), alkyd resins (Ferrario and Griffin, Windsor &Newton alkyd paint), an hydrocarbon resin (Regalrez 1094), an aldehyde resin (Laropal A81), and a polyethyl-oxazoline (Aquazol 500).

Characteristic pyrolytic profiles and mass spectra of significant pyrolysis markers were collected for each of the investigated materials. Principal component analysis was performed on the DE-MS spectra, proving this approach a useful tool for a fast and efficient comparison of the results obtained on raw materials, reference varnish layers and samples collected from works of art.

The proposed analytical methods do not require previous treatment of the sample, and, due to their high sensitivity, only a small sample amount in the microgram is recquired. This makes them particularly attracting for applications to works of art, to characterise new materials, and analyse samples of unknown composition.

Case studies relative to artworks from Keith Haring (Mural painting *Tuttomondo*, Pisa), Anselm Kiefer (*Die Grosse Fracht*, Biblioteca Comunale San Giorgio di Pistoia) and Fernando Melani (*Bandiera* and *Teatrino*, Museo Casa-Studio Melani, Pistoia) are discussed.

ABC-OR-08 “Sustainability” in conservation and restoration of the cultural heritage: considerations about the criteria in protecting and consolidating the architectural surfaces

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In the field of Cultural Heritage the propose introduction of "sustainable" technologies is becoming increasingly important, although it is not completely clear what is the meaning of "sustainability". This is often defined in terms of energy saving, but also a revival of traditional techniques and materials which are compatible with the artifact and, again, in terms of valorisation of the artifact itself [1, 2]. It is obvious that it is not possible to talk about sustainability in the context of Cultural Heritage without considering environmental sustainability, and vice versa. The system itself requires an complex evaluation: the use of materials and technologies which respect the human health and the environment; the revision of the criteria of efficiency of the conservation treatments; a larger attention to maintenance and monitoring of the artifact; the possible use of non-invasive techniques [3]; the evaluation of the impact linked the use and the tourism; the creation of databases accessible to the operator and the institutions responsible for safeguarding of the cultural heritage [4] , etc. This paper aims to analyze several different aspects associated to the definition of "sustainability" in the conservation and restoration of Cultural Heritage; in particular it takes into consideration the technological aspects linked to materials and methods currently used in the protection and consolidation of stone materials. The research wishes to propose a “numerical parameter of efficiency” defined by standard methods (as like UNI-Normal tests) but also in terms of environmental impact of the treatment in relation to the support, the safeguards of the operator, the expected duration of the treatment and the consequent maintenance operations.

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ABC-OR-09 Synthesis and characterization of wood-silica gel nanocomposites anchoring copper complexes active against biotic decay

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Interpenetration of wood samples of pine sapwood (*Pinus sylvestris* L.) with hybrid inorganic-organic silica xerogels bearing amine functions able to coordinate copper(II) cations has been successfully carried out. These materials have been prepared by sol-gel processing TEOS/APTES mixtures inside the wood. Solid state ^{29}Si NMR data provide evidence that the interpenetrated xerogel material has the same degree of condensation of the corresponding xerogel formed outside the wood. Copper(II) is effectively vehiculated inside the wood by coordination linkages with two ammine functions well evidenced by ESR measurements.

SEM/EDX investigations show that the chlorine/copper atomic ratio inside the wood is lower than that of the starting salt $CuCl_2$, suggesting an exchange reaction with silanol groups with the formation of Si-O-Cu linkages and HCl. This reaction could be promoted by the excess of amine functions with formation of ammonium chloride species which remain onto the surface of the wood and in the mother solution owing to a higher degree of condensation. The obtained wood treatments have shown high preservation performance against brown-rot fungi and subterranean termites, due to both the presence of copper and of the amino-functionalized xerogel [1]. The environmental impact of these preservatives also results lower than that of the commonly used copper formulations. This is due to the TEOS/APTES xerogel capability to reduce the amount of released Cu owing to an adequate fixation to wood, as demonstrated by 10-days lasting leaching tests.

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ABC-OR-10 A copper-containing metalloenzyme in tandem with a PQQ-dependent glucose dehydrogenase for monitoring phenolic compounds

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Recently we and others proposed an innovative method to make redox proteins suitable for sensing applications. The scheme builds on the translation of the binding event occurring at the enzyme cofactor binding-site into a change in the emission of a fluorescent probe covalently attached to the protein through a Förster Resonance Energy Transfer (FRET) mechanism. This principle has been advanced in the past few years for a number of applications based on oxygen detection by fluorescently labeled Type-3 copper proteins.[1-4] In the present contribution, the basic idea builds on the use of two enzymes that are coupled through a common substrate/product pair, *i.e.*, the product of the enzymatic activity of enzyme **1** is identical to the substrate of enzyme **2** and vice versa.[5] Co-substrates of the two enzymes are oxygen and glucose, respectively. In the presence of excess of oxygen and glucose, minute amounts of the common substrate/product are enough to ensure a continued cyclic reaction: instead of one turn-over by one enzyme a, in principle, indefinite number of turn-overs can be realized once a single molecule of the substrate/product pair is detected. The result is a large amplification in detection. The enzyme pair in our case consists of the copper-containing metalloenzyme tyrosinase (Ty) and the pyrroloquinoline quinone (PQQ)-dependent glucose dehydrogenase (GDH).[5] Ty converts mono- and di-phenols into quinones under consumption of oxygen, while GDH converts quinones back into the corresponding di-phenols under consumption of glucose. The challenge is to monitor the enzymatic consumption of oxygen as a function of the concentration of a mono- or di-phenolic compound. Recently Streffer et al reported the use of the Ty/GDH substrate-recycling couple as a sensor for phenolic compounds by monitoring the oxygen consumption with a Clark electrode.[6] Despite its numerous merits, the Clark cell is bulky and can be compromised by electrical interference.

The advantage in the present case is that we monitor the enzymatic consumption of oxygen by observing the fluorescence of a label that is covalently attached to the Ty.

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ABC-OR-11 Assessment of an ozone-based hygiene system for household dishwasher

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This work evaluates the oxidizing effect and antibacterial properties of ozone, related to the bacterial contamination control in the washing tub of the dishwasher. This concern is due to the fact that a dishwasher is not always operated immediately after its loading, which indeed may be partial load. Thus implying a time gap (some days) between loading and the start of the washing cycle in the appliance.

There is a difference of time in the loading and washing cycles. This is due to the energy saving and optimizing water consumption habits of the customer [1]. This induces a microbial degrading effect on the dishes due to the food residue leading to a smell inside the dishwasher.

Tests were performed on two identical dishwashers, of which one was equipped with an external device, generating ozone and pumping it into the washing tub of appliances [2], whilst the other one served as control. The system was configured with a suitable duty on/off cycle, aiming to reach less than 0.3 ppm ozone peak levels in the compartment and less than 0.1 ppm average. The two dishwashers were loaded in the same way with dishes spread with standard soiling agent that contains standard bacterial strains. A first step consisted of testing 3 standard soiling agent [3], each contaminated with an array of 3 bacterial strains, selected amongst 7 different strains based on trophic and metabolic characteristics. Every 24 hours, the soil were sampled from the dishes and analysed, to determine the variation of each strain's contamination. The two strains showing the most resistance towards ozone (*Pseudomonas aeruginosa* and *Listeria monocytogenes*) were selected for further analysis, consisting of two implanted non-standard soiling agents, showing the same traits as in the first step. A highly significant static bacteria effect was observed both for all the tested strains and for the types of soiling agents .With levels of bacterial contamination ranging 8% to 300% more in the control dishwasher than in the ozone dishwasher; the 2 strains showed different sensitivity to ozone action, with the substrate playing a probable role in affecting the sensitivity itself.

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ABC-OR-12 Polybrominated diphenyl ethers (PBDEs) in the atmosphere surrounding two WWTPs in Tuscany (Italy)

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Polybrominated diphenyl ethers (PBDEs) constitute an important group of brominated flame retardants that have been extensively produced and used in numerous everyday products. The market demand for PBDEs has been dominated by three major industrial formulations (penta, octa, deca-BDE mixtures), which are mixtures of tetra- to deca-congeners at various proportions[1,2]. The penta and octa formulations were banned in Europe in 2004, deca-BDE was also prohibited by July 2008. PBDEs enter the waste water treatment plants (WWTPs) from a variety of sources including urban and agricultural run-off, domestic wastewater, industrial point discharges, etc. and can be released to the atmosphere by volatilization and aerosol formation generated by bursting bubbles produced by the diffused aeration systems that provide oxygen to the microbial flora in the activated sludge processes. Thus, wastewater treatment processes are often overlooked as responsible for the emission of PM10 and associated pollutants. In this study, we collected PM10 samples in the inner and surrounding area (downwind and upwind) of two waste water treatment plants (WWTPs) in Tuscany (Italy), between 2004 and 2006, in order to determine the atmospheric occurrence and distribution of PBDEs and investigate WWTPs as source of these pollutants to the atmosphere.

PBDEs concentrations were compared to those found in samples taken simultaneously at reference sites that were not influenced by the WWTPs. Particulate and gas-phase samples were also collected to evaluate not only the gas-particle partitioning of PBDE, which is fundamental for assessing their fate and human exposure, but also to evidence temporal variations. Moreover, the risk of potential adverse health risks was calculated using the mean measured concentrations.

[1] van Esch, 1997
[2] UNEP; 2005

ABC-OR-13 Talitrid amphipods as biomonitors of PCBs and PBDEs contamination of supralittoral of sandy shores

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Coastal areas are characterized by a great input of environmental contaminants that can reach these zones by land based sources (including wastes from industrial, urban and agriculture activities, aquaculture, tourism), from sea based sources (oil spills, oil exploration and production) as well as atmospheric depositions. The contaminants of main concern include persistent organic pollutants (POPs), oils, fertilizers, heavy metals and pathogens[1]. Talitrid amphipods constitute one of the main animal components (in terms of biomass) of sandy beaches representing, moreover, a key species in the food web of these ecosystems[2]. In the last two decades, many species of sandhoppers and beachfleas have been successfully employed as biomonitor of trace metals contamination. In fact, studies carried out along European sandy shores have shown the ability of one of the most common Mediterranean sandhopper species (*Talitrus saltator*) to accumulate many trace heavy metals [3]. To date, no studies have been reported about POPs contamination of supralittoral of sandy shores and their presence in talitrid amphipods. In this study we analysed *T. saltator* collected from different coastal areas of Tuscany (Italy) looking for PBDEs and PCBs in order to verify if this species could represent a suitable biomonitor of POPs contamination of supralittoral of sandy shores. 20 PCBs and 9 PBDEs were identified in both sand and amphipods samples and their concentration in *T. saltator* was, for most part of PCBs and PBDEs congeners. Furthermore, results showed significant differences in bioaccumulation between amphipods form different localities. Therefore *T. saltator* could represent a promising biomonitor of PCBs and PBDEs contamination of the supralittoral band of sandy shores.

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[2] Bergerard, 1989
[3] Ugolini et al., 2005

ABC-OR-14 Humic substances dissolved and particulate in the system pack ice-superficial water in the Gerlache Inlet (Antarctica)

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Antarctic environment is a good "laboratory" to study natural processes in the environment because anthropogenic sources are absent. In particular, humification processes and the influence of algal bloom on marine humic compounds (HS) can be studied without the interference of alloctonous humic compounds because the input of terrigenous humic material is negligible. Nevertheless, because of the particular climate conditions, it is not possible to neglect the presence of pack-ice and their possible influence on the presence of humic compounds in water. In water humic compounds are present both as dissolved and particulate material and play an important role in the fate and transport of metal ions and organic pollutants. In particular, pollutants can be scavenged from water to sediments [1]or transported from sea to air from sea-salt aerosol, deriving from sea-surface microlayer, the interface between the ocean and the atmosphere. We have studied time to time humic substances present in superficial sea water both particulate (PHS) and dissolved (DHS) evaluating the influence of primary production on humic compounds (HS) concentration. Humic material recovered from Antarctic samples consists only of fulvic acids both dissolved (DFA) and particulate (PFA). All data confirm that PFA are younger than DFA and richer of nitrogen containing groups, even if aromatization and condensation processes are not in an advanced stage. The primary production increases the amount of particulate matter with a consequent decrease of the PFA percentage. In a successive time begins the humification process, but at the same time it is in progress the sedimentation process owing to particulate matter shifts along water mass into deep layers. Consequently in superficial water the PFA concentration depends both from the primary productivity and from the sedimentation rate, whereas when pack ice is present the PFA concentration depends both from the ice melting and from the sedimentation rate. DFA are only slightly influenced from primary productivity.

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ABC-OR-15 Principles and application of Industrial Ecology for a sustainability of the waste management system

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The principles of Industrial Ecology are inspired by the integration of green chemistry and green engineering. Some key ideas can be defined: - system analysis, i.e. a wide vision of interrelations among human activities and environment; - flows and transformation of matter and energy; - multidisciplinary approach; - analogy with natural systems; - closed cycles vs. open cycles.

Some basic elements are:

Ecodesign: an approach to the design of products and services in which environmental issues are considered from the beginning of an industrial supply chain: reduce materials, energy consumption, toxic substances; and increase recyclability, use of renewable resources, product durability.

Life Cycle Thinking: to see products and processes from a life cycle standpoint.

Flow Analysis: to map and quantify used and discharged materials by a user network (companies, industrial districts, regions, supply chains...)

Industrial Symbiosis: based on the idea of exchange, where the wastes of a company are inputs for other producers.

Green Policy: actions and directives aimed at promoting environmental sustainability (Environmental certification, Extended Product Responsibility, Product to Services...)

The sustainability in waste management sector is strongly affected by these innovative concepts. In order to create a European recycling society, within 2020 Member States are called to achieve targets of 50% for household waste and 70% for construction & demolition wastes. The Ecodesign approach could highly influence the production of sustainable, reusable and recyclable goods.

From a technical-scientific perspective, an integrated waste management system must be followed by the application of different tools: monitoring of waste flows, their composition and physic-chemical features, implementation of best treatment and disposal techniques. Furthermore, validation approaches must be applied, as LCA, Risk Analysis, and integrated environmental monitoring system.

The final scope is to reach a definition of a practical waste management system for each area, in relation to specific territorial features.

ABC-OR-16 A new (OPIE + OPEE) device for simazine and atrazine analysis in olive oil

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To complete the research begun last year, several tests were carried out concerning the possibility of fabricating immunosensors working in organic solvents mixture (OPIE) and aimed at developing new immunosensors for the analysis of triazinic pesticides present in hydrophobic matrices such as olive oil.

Initially, an immunosensor for atrazine was tested in which a hydrogen peroxide electrode was used as transducer and peroxidase enzyme as marker. The competitive process took place in the chloroform-hexane (50% V/V) mixture while the subsequent enzymatic measurement was performed in an aqueous buffer solution. A linear response of between about 50 nM and 5.0 μM was obtained versus atrazine, in presence of olive oil. Subsequently, attempts were also made to use a Clark electrode as transducer and to perform not only the competition but also the final enzymatic measure in organic solvent, such as for the OPEEs. The latter enzymatic measurement was therefore carried out in several different organic solvents, such as decane, hexane, chloroform and chloroform-hexane mixture. The best analytical results were obtained using decane as solvent and tert-butylhydroperoxide as substrate of the enzymatic reaction. As far as measurements of K_{aff} using the Langmuir curves are concerned, the latter value was found to be equal to about 10^6 M^{-1} in all tests performed in the presence of the oil phase and about 10^7 M^{-1} in the absence of the oil phase. These values show that even when the antibody reaction occurs in organic solvent, antibody complex formation takes place more than satisfactorily and allows an immunological method to be developed properly. Selectivity of new immunosensor was found to be similar to the same device studied in previous work, but operating in aqueous medium. It was pointed out that when using the same antibody as that used also in the present research, the only interferents are practically simazine and to some extent terbuthylazine and buthylazine desethyl. Also the response to non triazinic pesticides was tested. For this type of pesticide (organophosphorus and carbamates) the response was found to be extremely low, although non negligible. In the case of simazine it was found that the calibration sensitivity is 40-50% lower than that of triazine although the linearity range and the LOD are of the same order. It is thus possible to analyse also this pesticide, which is also the one most frequently found in olive oil samples. The observed data showed that in practice traces of triazinic pesticide, probably simazine, were found only in two out of the four extravirgin olive oil samples tested. Lastly, recovery tests carried out on extravirgin olive oil spiked with atrazine always yielded recoveries in the vicinity of 100%.

ABC-OR-17 Study of the stability and reactivity of sulfur compounds against copper in dielectric insulating fluids: definition of a corrosiveness ranking

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Failure events in large power electrical apparata for energy generation, transmission and distribution are of extreme interest, since they can cause either socio-economical (interruptions of power energy supply, civil black-out, lose of production in industrial plants) or environmental (explosion, fire, pouring of dangerous compounds) consequences. In the last years, several failure events have been ascribed to the presence of sulfur based compounds inside the insulating liquids used for the impregnation of power transformers. While some sulfur compounds show antioxidant properties (such as thiophenes and their derivatives), others may induce corrosion phenomena against Cu of the windings' conductors.

The aim of this work is the study of the stability and the reactivity of classes of compounds (aliphatic and aromatic mercaptans, sulfides, disulfides, thiophens) which could be present in the insulating liquids of transformers in service, as a result of poor refining, back-blending or addiction. To fulfill this task, nine compounds representative of the above mentioned classes have been selected: dodecylmercaptan, hexadecylmercaptan, benzylmercaptan, butyldisulfide dibenzylsulfide, phenylvinylsulfur, phenyldisulfide, dibenzyldisulfide, dibenzothiophene. Their stability has been firstly investigated as a function of temperature (80-200 °C) and of ageing time (36-288 h) with or without oxygen, to simulate the natural ageing of either hermetically sealed or free breathing type transformers. Subsequently, their reactivity against Cu has been investigated, by repeating the experiments in the presence of Cu strips. The amount of each sulfur compound was quantified by a GC-AED (atomic emission detection) method, optimized for the purpose. Several on-sites investigations on failed transformers revealed that the formation of Cu_xS_y on the Cu conductor surface and onto the adjacent insulating paper tapes was involved in the failure mechanism. To investigate the corrosiveness of different sulfur compound families, the conversion of 22 sulfur compounds to Cu_xS_y was studied as a function of temperature in the presence of Cu. The total sulfur amount was determined by nephelometry after the oxidation of sulfide species to sulfate. The data obtained allowed us to define a corrosiveness ranking for the families of compounds tested, which was proven to vary with temperature. In particular, for T between 80-120 °C, mercaptans are the most corrosive compounds, while for T between 150-180 °C, the highest corrosiveness properties are exhibited by disulfides.

ABC-OR-18 An organo-zeolite for environmental applications

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A novel organo-zeolite material for water purification from organic pollutants has been developed and characterized. A sample of a phillipsite/chabazite-rich tuff (PCT) coming from a quarry near Naples, with grain size ranging between of 0.5 and 1.0 mm, has been initially full enriched in calcium ion. Afterword, the Ca-PCT sample was eluted with a solution of humic acids (HA) in a chromatography column (HA solution concentration = 100 mg L-1, pH = 7.4, flow rate = 1.0 mL h-1). HA are natural organic polymers containing aromatic blocks and are produced by the biological decomposition of organic matter from plants and other organisms. HA is the main component of the organic matter of surface water and of the soils. They are soluble in water at neutral and basic pH, moreover, they are able to adsorb hydrophobic compounds in their core within their molecules. In previous studies [1] we have shown that the phillipsite-chabazite-containing tuffs are able to bind HA and that the binding ability was markedly enhanced when the zeolitic material was enriched with divalent cations, especially Ca2+. In line with this result, the elution on Ca-PCT of HA solution produced an organo-zeolite adduct with a content of approximately 3000 mg of HA for kilogram of tuff. The solubility of the adsorbed HA was markedly decreased by treatment with a 10 % glutaraldehyde solution followed by heating at 330 °C for 1.5 h and the composite material so obtained was tested for adsorption of organic compounds. The figure reports an adsorption test carried out eluting a column of HA-Ca-zeolite adduct or zeolite alone eluted with a phenol solution, 220 mg L-1. The comparison between the breakthrough curves for the organo-zeolite combination and for the zeolite alone highlights the excellent adsorbing properties of this inexpensive, easy to prepare and environmentally-friendly novel material.

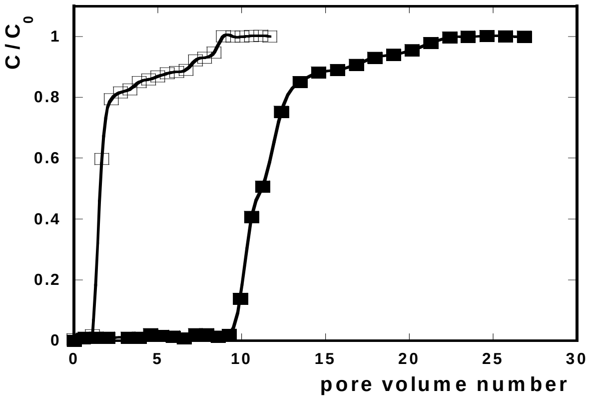

Figure: Breakthrough curves for the adsorption of phenol on the (■) immobilized HA on zeolitic tuff and on (□) zeolitic tuff alone.

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ABC-OR-19 Adsorption of pharmaceuticals from water by zeolites

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A large amount of pharmacologically active substances are used yearly to treat human and animal illnesses, in farming and aquaculture. These substances can be excreted unmetabolized or as active metabolites; they can escape degradation in sewage treatment plants and can be detected in sewage, surface, ground, and drinking waters. Improper disposal of expired medications also contributes to this contamination. Atenolol (β-blocker) and hydrochlorothiazide (diuretic) have been detected in several sampling sites along rivers Po and Lambro: these two drugs are poorly metabolized in humans, and are therefore mainly excreted as parent compounds (90-95%) [1].

Many drugs don't exhibit an acute toxicity but have a significant cumulative effect on the metabolism of non-target organisms and ecosystem as a whole, showing specific pharmacological and physiological functions [2].

Zeolites are microporous aluminosilicate minerals which combine a well-defined crystalline structure, including regular void spaces (pores and cavities), with well-defined functional groups generated by the controlled substitution of elements into silicate or aluminumphosphate lattices. These materials can be used as alternative sorbent materials for several classes of contaminants such as hydrocarbons, MTBE and also pharmaceuticals.

In this study, the retention of atenolol, ketoprofen and hydrochlorothiazide on three types of zeolite Beta is investigated. The zeolites differ from each other in hydrophobicity degree (different Si/Al ratios). To accomplish this task, the adsorption properties are characterized by adsorption isotherm determination; the influence of both ionic strength and pH on the adsorption properties are single out. Since the knowledge of the mechanisms governing zeolite/pharmaceuticals interaction can be helpful for the potential use of these minerals in wastewater remediation, structural and thermogravimetric measurements are carried out to investigate the role of the zeolite structure on the drug retention. The results demonstrate that Beta zeolite show fast adsorption kinetics and good removal properties for the studied drugs.

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ABC-OR-20 A methodological approach for the development of a guideline for odour emissions and odour impact evaluation

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In the perspective of the improvement of life quality and citizens wellness, odour pollution is becoming a more and more relevant topic. In fact, among the variables that could influence the citizens sense of a healthy environment, odour emissions play an important role, as they deeply affect the human life quality and psycho-physical wellness [1]. The increasing attention of the population to olfactory nuisance and the proximity of industrial plants to residential areas have generated the need of evaluating odour impact and regulating odour monitoring and control. Odour emission monitoring and its regulation are characterized by a great complexity due principally to the strict association of odour pollution to human perception. In order to establish a proper management and policy for odour emissions, different approaches have been developed [2] but they do not adequately satisfy the requests of monitoring and control expressed by the population directly exposed.

In this work, a proposal of a methodological approach for an odour guideline is presented with the purpose of defining acceptability and monitoring criteria for odour emission produced by industrial activities. According to the principle of pollutant prevention and reduction, commonly adopted by environmental legislations, the present methodology suggests a coupling between a predictive approach, based on dispersion models, and a systematic approach to carry out the monitoring and the control through reliable methodologies [3]. The novelty of the proposal is represented by the introduction of a buffer zone, individuated by means of dispersion models, in which prescriptive limits have to be fulfilled and verified by standard measurement methodologies. In addition, the odour guideline recommends to perform a process control for particularly impactful plants, realized through continuous monitoring systems.

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ABC-OR-21 Testing different treatment strategies for the treatment of municipal landfill leachate

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Municipal landfill leachates, resulting from the percolation of water through solid waste, represent an environmental issue due to their toxic potential [1]. Their treatment should include advanced oxidation processes (AOPs) after a biological step.

The treatment of a medium-age landfill leachate was investigated by employing several set-ups including a sequencing batch biofilter granular reactor (SBBGR) step [2], with or without ozone enhancement, followed or not by a polishing stage with solar photo-Fenton (SphF). Objectives of the investigation were to compare different treatment strategies in order to achieve the lowest operating cost and to reduce the toxicity of the final effluent, evaluated by three different tests (respirometry, *Vibrio fischeri* and *Lepidium sativum* phytotoxicity). These objectives were addressed for two different target COD values, namely 160 and 500 mg/L, to be met in the final effluent for disposing of to water bodies and to sewers, respectively, requested by Italian environmental regulation. The different treatment strategies have demonstrated to be technically suitable for achieving the requested COD (160 or 500 mg/L) and initial toxicity reduction (using three different bioassays) goals. For the COD target of 500 mg/L, the two investigated treatment set-ups showed to have comparable operating cost (3.2 €/$m^3_{inf.}$).

Instead, when the target COD is 160 mg/L, the combination SBBGR+SphF is economically more convenient (4.1 €/$m^3_{inf.}$) being the operating cost of the other two investigated treatment set-ups (SBBGR/O_3 and SBBGR/O_3+SphF) 5.7 and 4.8 €/$m^3_{inf.}$, respectively. As for toxicity reduction, for both the COD target of 500 and 160 mg/L, the SBBGR/O_3 set-up gave better results than other treatment options.

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ABC-OR-22 Atmospheric pollutants deposition flow close to a municipal solid waste incinerator: 5 years-monitoring results.

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In Italy, Municipal Solid Waste (MSW) treatment represents an issue of persistent concern. Even though more stringent emission limits for incinerators have been established (2000/76/CE directive), and the implementation of *best available techniques* should ensure low environmental impact, local contribution of pollutants in atmospheric flux depositions could be not negligible. Among these, persistent organic pollutants (POPs), such as polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) or polychlorinated biphenyl (PCBs), and heavy metals (HM) generate the greatest alarm.

The aim of this study is to estimate the relative contribution of a MSW incinerator to the pollutants burden in the surrounding area. To do that, organic (PCDD/Fs, PCBs, PAHs) and inorganic (Cd, Cr, Cu, Ni, Pb, Mn, Zn and As) pollutants have been determined in different samples of atmospheric depositions and soil.

The plant is located in a sub area, not far from a tourist town (Riccione), an important Italian highway (A14), and the Adriatic coast. It was opened in 1976; it increased its capacity to 127.000 tons/year in 1992. The plant was revamped in 2008 and for this reason, it shut down its activity for about six months and it operated at reduced capacity for the following six months.

Monitoring network was drawn on the basis of the dispersion map of incinerator stack emissions, calculated by the atmospheric dispersion model *Calpuff*. Sampling sites (5) were located in zones affected by different incinerator emissions fallouts.

From 2006 to 2010, bulk atmospheric deposition samples were collected monthly for heavy metal analysis and at intervals of about 6 months for organic pollutants analysis, whereas soil samples were collected once a year.

Results show that the studied area is subject to low contamination, as far as these compounds are concerned. Deposition flows show neither higher pollutants burden at sites most affected by emission plant fallouts, nor differences in deposition flux during the plant switch off. Furthermore, soil contamination seems to be more influenced by the nearby urban area emissions, than those from incinerator.

In conclusion, study area is apparently characterized by a homogeneous and widespread contamination that cannot be ascribed to the only incinerator emissions.

ABC-OR-23 Biogenic Volatile Organic Compounds from trees in the province of Trieste (NE-Italy)

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Within the Province of Trieste, anthropogenic emissions of Volatile Organic Compounds (VOCs) from trafic, steelwork and a crude oil tankfarm have previously attracted attention for toxicology and odour nuisance assessment. Vegetation contributes to VOC emissions budget, and atmospheric oxidation of these Biogenic VOCs contributes to new particle formation and atmospheric organic aerosol mass [1].

A study was started for the evaluation of BVOCs emission from major tree species spread over the Province, and deciduous *Quercus ilex* and *Quercus pubescens,* as well as evergreen *Pinus niger* were considered. Experiments allowed to identify α-Pinene, β-Pinene, Camfene e R-Limonene, β-fellandrene and δ-3-carene, among other compounds.

BVOCs emission rates were determined by dynamic branch enclosure with active samplers, at different times. Experimental data are aimed also at supporting validation of computational models, as Model of Emissions of Gases and Aerosols from Nature (MEGAN) [2], or Biogenic Emission Model (BEM) [3], that can be used for PM and ozone impact management.

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ABC-OR-24 Particle-Phase Polycyclic Aromatic Hydrocarbons in the Venice area: The relative importance of local emissions and Transboundary Movements of Air Masses. Preliminary Results

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In the atmosphere, the high m.wt. Polycyclic Aromatic Hydrocarbons (PAHs) are mainly present in the particulate phase and many of them are recognized having carcinogenic effects. The concentrations of 11 particle-bound PAHs were measured in the Venice-Mestre atmosphere. In this area, the air quality is affected by local anthropogenic emissions [1,2], but a strong influence of regional-scale transport of pollutants was recently detected as well[3].

A sampling campaign of fine particulate matter ($PM_{2.5}$) has been extended for one year in three sites selected to be representative of different emissive scenarios: urban background, industrial fall-out and semi-rural coastal site. PAH contents were determined using GC/MS after solvent extraction and liquid–solid chromatography clean-up. In addition to the identification of the most probable emission sources using common approaches, the main goal of this study was to test a procedure to assess the relative importance of local air circulation and regional-scale transports on PAHs levels. A first factor-cluster analysis [3] was performed to highlight the impact of local sources evaluating the relationship between variations of PAH levels as a function of wind speed and direction. Results revealed a strong influence of locally generated processes and atmospheric circulation on PAHs levels. In particular, the absence of significant advective transport episodes resulted in severe pollution events due to the accumulation of local anthropogenic emissions.

The variations in PAH levels were also related to backward air mass trajectories to trace the history of air masses and the potential impact of regional-scale transports. Results evidenced that the levels of PAHs increased when air masses came from Eastern Europe and spent most of their time over the Po Valley. Conversely, pollutant levels had dropped when the origin of trajectories was North and Northwestern Europe.

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ABC-OR-25 Harmful algae in the Venice Lagoon and in the Po River Delta (northern Adriatic Sea, Italy)

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An integrated approach for the structural identification and quantification of algal toxins, in Northern Adriatic Sea, specifically in the Po river delta and in the Venice lagoon, by applying a combination of analytical techniques such as optical and scanning microscopy (OM, SEM), and Liquid Chromatography coupled with High Resolution Time of Flight Mass Spectrometry (HPLC-HR-TOF-MS), is presented. The proposed approach has been preliminary applied to the investigation of harmful algae occurrence and distribution in the above mentioned coastal areas.

The performed sampling sessions showed that potentially harmful algae such as *Dinophysis caudata*, *D. mitra* and *D. sacculus* were present during summer period in most of areas directly influenced by seawater, such as the Venice port entrances and the Po river delta, but not in the inner Venice lagoon parts.

Nevertheless, quantitative observations demonstrated that their abundance were always significantly below the conventional limit (~200 cells/L) for which poisoning events could occur [1]. The presence of Pectenotoxin2 (PTX2) in phytoplankton cells extract was anyway confirmed by HPLC-HR-TOF-MS at Venice lagoon port entrance, so indicating the potential release of toxins in detectable amounts even at such low cell concentration levels [2, 3].

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ABC-OR-26 Importance of the particulate matter ionic fraction in the planning of data centres for the prevention of corrosion

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The planning and construction of Data Centre with Direct Free Cooling by using outdoor air as direct fluid of heat transfer inside the computers, consents to obtain a fuel saving in the conditioning phase, which translates less environmental impact; however, the legislation (ASHRAE 2009) [1] requires monitoring of air quality, with particular reference to concentrations of particulate matter and its hygroscopic properties, in order to prevent corrosion phenomena in the computers. The study focused on the planning of the ENI Green Data Center located in Sannazzaro dé Burgondi, in the middle of the Po Valley at the same named refinery and tubogas station with combined cycle ENI 1 GW. Two measurement campaigns were conducted (during winter and summer) at the Sannazzaro de Burgondi site near EniPower. $PM_{2.5}$, PM_1 e $PM_{0.4}$ samples (FAI-Hydra dual channel) were collected in conjunction with measurements of its number concentration and dry and humidity size distribution through the use of an OPC-Tandem (OPC GRIMM 1.107 *"Environcheck"*) and with measurements of the mainly meteorological parameters. The particulate matter samples were analyzed using ionic chromatography (Dionex ICS-90 e ICS-2000) in order to determinate the inorganic ionic fraction (Na^+, K^+, Ca^{++}, Mg^{++} NH_4^+, F^-, Cl^-, NO_3-, $SO_4^=$) and the organic one (mono and di-carboxylic acids). The PM ionic fraction analysis allowed the determination of its deliquescence using the application of a thermodynamic model of phase partition: the Extended *AIM* Aerosol Thermodynamics Model [2] (http://www.aim.env.uea.ac.uk/aim/aim.php). The deliquescence point was on average 60% greater than RH%, both through simulation modelling and experimental measurements (Tandem-OPC), thus favouring the presence of dehydrated aerosol in the thermodynamic operating conditions of the data centre (298.15 K, 10-60% RH%), condition that prevents the onset of corrosion related to the deliquescence of the particulate matter.

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ABC-OR-27 Airborne Particulate Matter in Apulia Region: features and critical episodes

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Airborne particulate matter (PM) is a complex mixture of particles which show substantial differences in size, chemical properties and thus in the toxicological and carcinogenic effects they cause. Several epidemiological studies, in fact, suggested the relevant role of PM concentration in contributing to a range of health effects [1]. Based on these implications on public health, many countries have developed plans to suggest effective control strategies which involve the identification of PM sources, the understanding of PM transport, mixing and transformation processes and the identification of the main factors influencing PM concentrations.

In this work, the results obtained by applying an integrated approach in PM monitoring campaigns are shown. The integrated prototype denominated 'SIMPA' consists of a Swam dual-channel sampler, an OPC Monitor, a sonic anemometer and a PBL Mixing monitor. The high time resolution of data and many information produced by the prototype allowed to identify the contribution that one source gives to the particulate matter concentrations respect to the bottom of the surrounding environment, and to identify optically particle size range of particles involved in the localized emission sources. The data collected in different sites in Apulia Region have allowed to identify different 'indicators' for the characterization of PM sources. PM2.5/PM10 ratio, daily mean values of natural radiation, particle numerical concentrations for the most significant optical diameters were considered. These informations, the chemical characterization of filters, the weather data and the information obtained by aerosol models such as HYSPLIT and DREAM, have allowed to evaluate the contribution of local anthropogenic sources, long-range transport from East Europe and African dust outbreaks. Finally, the obtained results were confirmed by applying Principal Component Analysis (PCA) to the numerical particle concentration dataset. It allowed to identify samples characterized by coarse mode of aerosol particles (natural events) and the accumulation one (anthropogenic events).

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ABC-OR-28 Characterization of PM10 of three different site by analyzing individual particles

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SEM/EDS was applied to study the chemical and morphological parameters of PM particles. Considering both the parameters, the study and evaluation of the effects of many processes can be adequately done, i.e. the absorption of volatile molecules present in atmosphere, chemical reactivity and not least the origin of the particles. In particular, in literature some studies have been concerned to relate the composition and morphology of particulate highlighting the special relationship with atmospherical conditions.

In this work the PM10 samples, collected by a low volume sequential sampling on polycarbonate membranes, belong to three sites characterized by different boundary conditions: a yard site, an urban site and a rural site. In this work a protocol for the morphochemical characterization of single particles has been developed. Morpho-chemical characterisation of particles was performed by ESEM - EDS microanalysis: 20 chemical parameters (C, O, Na, Mg, Al, Si, P, Cd, Cl, K, Ca, Sn, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn) were determined and 7 morphological parameters (area, aspect ratio, roundness, fractal dimension, box width, box height, perimeter) were measured by Image Pro Analyzer 6.3. A set of 1340 particles from three sites has provided three sets of structured data in a poly-dimensional matrix (27 variables x 1340 particles).

Results revealed the presence of different clusters of particles, differentiated on the bases of chemical composition and morphological parameters (aluminosilicates; calcium particles; biological particles; soot; cenosphere; sodium chloride; sulphates; metallic particles; iron spherical particles).

ABC-OR-29 Interactions between cinnabar (HgS) and proteinaceous binders in paint-layers studied by Thermoanalytical (TGA) , Spectroscopic (FTIR) and Chromatografic techniques (SEC)

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Paints layers are generally made up of one or more pigments, which are a fine powder of inorganic coloured minerals, and a fluid binder, which enables the pigment to be dispersed, and to adhere to the support.

Historically, binding media were natural products from plants or animals, including protein-based materials such as egg, casein or animal glue, vegetable gums, drying oils, and natural waxes. These could be used alone or in mixtures, determining the different painting techniques. Egg proteins have commonly been used as binders, in the “tempera” painting technique. The organic paints constituents, and thus proteins as well, undergo to phisico-chemical modifications which are referred to as "ageing", leading to the formation of new functional groups and intermolecular and intramolecular bonds. This work aims caracterizing the interactions between ovalbumin and casein and the pigment cinnabar (HgS) in paint layers and how these evolve with time. The degradation of proteinaceous materials was also investigated.

The research was carried out on a set of paint replicas on glass slides freshly prepared, which were analysed fresh and after artificial light ageing. Multiple physical-chemical techniques were used, including Thermogravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR) and size exclusion chromatography coupled to UV and cold vapour generation atomic fluorescence spectrometry (SEC-UV-CVG-AFS). TGA, FTIR and conventional SEC have been widely used in the field of cultural heritage showing that these techniques are of primary importance for the comprehension of structural changes of binders during aging in the presence or not of other organic and inorganic materials [1]. SEC coupled to CVG-AFS detector is instead a novel approach for the comprehension of the protein-mercury interactions [2].

TGA and SEC allowed us to highlight the occurrence of interactions between proteins and pigment, and permitted to partially investigate into their nature and evolution with ageing. In particular we found that cinnabar forms stable complexes with both albumin and casein. Moreover the most part of mercury resulted to be associated with albumin monomer in not aged samples and with the high MW fraction in aged samples. On the other hand, in casein samples, cinnabar is complexed only with the high MW species both in not aged and aged paint replicas.

FTIR proved to be useful for chemically characterise the modifications undergone by the proteinaceous binders alone and in the presence of pigment, as an effect of light ageing. In particular FTIR spectra of aged samples showed data consistent with oxidation and hydrolisis of the proteins.

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ABC-PO-01 Use of the macroalgae of Orbetello lagoon for biofuels production

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The Orbetello lagoon is an important site for fish farming activities and in recent years there has been an excessive macroalgal growth that caused serious problems to the entire ecosystem. Two actions have been undertaken to reduce the ecological impact: the installation of pumps in order to increase water exchanges between the sea and the lagoon, and the harvesting of macroalgal biomass. This last activity is executed every year from May to November by boats collecting approximately 40 t per day of two dominant species: *Gracilariopsis longissima* and *Chaetomorpha linum*. Also *Ulva sp.* was present and collected for analyses. Until now the algae are transported and confined in a landfill, with very high annual cost. We analysed the potential production of oil from the 3 species considered as waste.

The aim of this work is to evaluate the lipid composition of macroalgae from Orbetello Lagoon (southern Tuscany, Italy) in order to produce biodiesel

Lipid extraction was carried out according both to Bligh and Dyer method and using a Dionex ASE200 (Accelerated Solvent Extractor). The total lipid content was determined by microgravimetry and the fatty acids by GC-FID and GC-MS after acid transesterification.

No statistical differences were found between the two extraction methods, lipid concentrations were higher in *G. longissima* than in *C. linum* and *Ulva sp.*

Fatty acids compositions were similar in the three species with C16:0 as dominant compounds. Generally, lipid contents and profiles of Orbetello Lagoon's macroalgae were comparable with those reported in the literature for the same species. The macroalgal fatty acids corresponded to those normally constituting the biodiesel.

The results demonstrate that by improving the oil extraction methodology, macroalgae could be considered a good residual biomass for biofuel production.

ABC-PO-02 Colloidal AgNP for LSPR based glucose-sensor

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Gold and silver nanoparticles have been widely used during the past years in various technical and biomedical applications [1, 2].

In particular, the resonance optical properties of nanometer sized particles have been employed to design biochips and biosensors used as analytical tools.

The dependence of the resonance condition on the local dielectric environment enables a simple form of molecular sensing in which analyte binding to the nanoparticles surface causes a shift in the spectral extinction peak [3].

Furthermore, nanoparticles have a highly localized LSPR sensing volume which eliminates the need to trap the interacting molecules of interest in a polymer matrix to enhance the signal, as is often done in SPR measurements. In this work, silver nanoparticles in ethanol have been synthesized by using poly(vinyl alcohol) as capping agent. The obtained nanoparticles have been analyzed by transmission electron microscopy methods in order to optimize the synthesis method to obtain monodisperse particles, in particular, the poly(vinyl alcohol) concentration has been calibrated in order to avoid particles agglomeration. Then the optical properties of the silver nanoparticles in solution have been analyzed and a progressive shift of LSPR caused by the adding of increasing quantities of glucose has been observed. High Resolution Electron Microscopy (HREM) shows the presence of superstructures onto the silver nanoparticles surface imputable to glucose.

The LSPR nanosensor developed in this study is expected to demonstrate a wide range of biomedical and environmental applications [4]. Its simplicity and low cost will make it accessible to the public, which could revolutionize medical diagnostics and medical economics. While the commercially available SPR biosensor has some of these capabilities, a nanoparticle based sensor could improve both medical diagnostics and biomedical research by easily diagnosing large numbers of biomolecules quickly.

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ABC-PO-03 Microstructural investigations of archaeological pottery from site of Mersin-Yumuktepe (Turkey)

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The great potential of synergy between archeology and scientific disciplines for the study of artifacts of historical and artistic interest is undeniable. The primary purpose of a scientific approach to archaeological objects is their conservation, preservation and study of knowledge and technologies in place for their production. Such information are essential to assess the cultural and technological aspects of past societies.

In particular, the use of scientific techniques allows to study the chemical composition of products, obtaining important information on identity and origin of raw materials. In addition, these data can help assess the commercial trade or exchange of artifacts between cultural groups, the technological capabilities and development, working conditions and living conditions, social customs and the differentiation features of the products on the destinations.

n present work, this multidisciplinary approach was applied to study some bricks that are part of the remains of the walls of some buildings found in site of Mersin-Yumuktepe, on the Southern coast of Anatolia, and from two different historical contexts: Neolithic and Chalcolithic.

For this purpose, we have used a scanning electron microscope, equipped with X-ray microanalysis system energy dispersive (SEM-EDX), and an X-ray diffractometer (XRD) in order to assess the morphology, the majority elements (Si, Ca, Al), the minority elements (Fe, Mg, K, S, Ti, P, Na, Cr) and the crystallographic phases. Moreover, it was possible to determine possible crystallographic changes and to reconstruct the evolution after any thermal annealing.

The experimental results obtained from these bricks, were compared with other pottery samples found previously in the same site, by using PCA (Principal Component Analysis), in order to highlight the presence of possible common sources of supply of raw materials for manufacture of different use.

ABC-PO-04 Study of the *patinas* on the Medieval bronze door of the cathedral of Troia (Foggia, Apulia)

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In Europe there are about thirty specimens of Medieval bronze doors, all made in the early years of the eleventh century and the mid-thirteenth century.
Many of these ports are located in Southern Italy and five can be observed in Apulia. In particular, a door (dated 1076) is the sanctuary of St. Michael the Archangel at Monte Sant'Angelo, a door (made in the eleventh century) is at Mausoleum of Boemondo d'Altavilla in Canosa, a door (made during the main phase of construction of the cathedral, completed by 1186) is at Cathedral of Trani. This door, recently restored, is now kept inside the temple.

The remaining two bronze doors can be seen at the Cathedral of Troia and they are both the work of Oderisio of Benevento: the main door was commissioned by bishop Guglielmo II in 1119 and the secondary door, located in the southern side of the Cathedral, is dated 1127. In 1127 in the city of Troy was celebrated a council convened by pope Onorio II and the secondary door is made of carved panels, enclosed by simple frames with inscriptions that sing the praises of the bishop Guglielmo II.

In this paper, we have reported the experimental results of non-destructive analysis performed on the *patinas* of the second door of the Cathedral of Troia.

In order to carry out this archaeometric study, we have used a portable apparatus of Energy Dispersive X-Ray Fluorescence (EDXRF).

ABC-PO-05 Study of XIX-XX century pigmented filler of tombstone inscriptions of the Monumental Cemetery *Villetta* of Parma

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The *Villetta* of Parma is the urban cemetery dating back to the beginning of XIX century at the time of Maria Luigia of Austria government. Designed as a city with orthogonal streets and chapels, it is rich in memorial monuments of great value for Parma history. The inscriptions show ancient prayers, signatures, dedications that reflect a singular approach to the commemoration ofthe dead person no longer in use. The materials used for making inscriptions have not been widely studied yet: their knowledge is important to understand ancient recipes and to identify suitable conservation treatments. This work is focused on the study of pigmented pastes filling carved inscriptions preserved both along the Portico and inside the Galleries of the monumental cemetery. They show heterogeneous conservation conditions up to the loss of legibility. The Raman spectroscopy analyses resulted the main useful technique to characterize these particular pastes and their alteration products; the obtained results were confirmed by micro-FTIR spectroscopy (ATR) and elemental analysis coupled with the scanning electron microscope. Black pastes, based on Carbon and Calcite, grey pastes, Carbon and Barium Sulfate, and red one of Hematite were found on white marble tombs; gildings on gypsum-based preparation layer and more recently yellow paste made of lead chromates were used on slate and other dark stones.

Organic material, ranging from paraffin waxes to proteins and lipidic substances, were also identified. Most of the originally black inscriptions have changed to green due to the formation of copper compounds such as Atacamite/Paratamite, antlerite, copper oxalates (Moolite) [1] copper and zinc metal soaps. The gilding layers have detached leaving out the gypsum-made preparations. The stratigraphy of many pastes allowed to recognize the subsequently added materials: paraffin waxes, modern painting layers made of Rutile and lead chromates. The conservation planning in the monumental area of *Villetta* in Parma has been defined thanks to the collected data.

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ABC-PO-06 Pd-Nanoparticles catalyzed one-pot sequential Heck and Suzuki couplings of bromo-chloroarenes in ionic liquids and water

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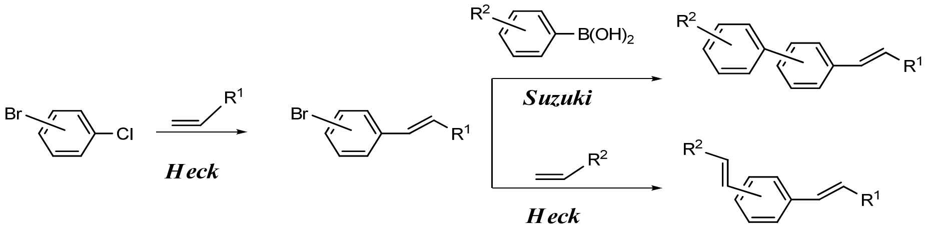
The Pd-catalysed cross-coupling strategy has gained considerable attention as a straightforward method for the synthesis of highly conjugated systems such as polyenes, aryl polyenes, and polyaryls, that are a common structural motif in many products.[1] In pursuit of this objective, several authors has been attracted by the potentiality of the sequential multiple couplings strategy involving the well-known Heck, Suzuki, Stille, etc. reactions, because these processes are usually high-yielding, stereoselective and tolerant towards a wide array of functional groups.

However, in many cases this approach can suffer from some disadvantages often requiring two different catalysts or the isolation of the intermediate product. One very attractive variant can be the one-pot double coupling of commercially available dihaloarenes, performing the consecutive coupling in the same reaction flask and in the presence of a single metal catalyst. There are only a handful of reports of such reactions on polyhaloaromatics, and in most of them the more reactive iodo/bromoarenes are usually preferred as substrates, while the cheaper and challenging bromo/chloroarenes are unexploited, with few exception,[2] due to the hard activation of the C-Cl bond.



As a result of our recent success with simple chloroarenes, [3] we report here that Pd nanoparticles generated in green reaction media (viz. ionic liquids and water) can catalyze the one-pot sequential Heck and Suzuki coupling reactions of bromo-chloroaryls to afford unsymmetrically substituted arenes in good yields.

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ABC-PO-07 Metal concentrations in Mediterranean blue mussels and evaluation of the mussels quality and possible risks of high human consumption

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Urban and industrial activities introduce large amounts of pollutants into the marine environment, causing significant and permanent disturbances in marine systems and, consequently, environmental and ecological degradation. This phenomenon is especially significant in the coastal zones that are the main sinks of almost all anthropogenic discharges of pollutants. In marine environment the persistent inorganic elements (e.g. metals) and organic contaminants (e.g. POPs and PCBs) are global issue, since continuous exposure of marine organisms to their low levels may result in bioaccumulation, and subsequent transfer to man through the food web. Although trace metals are normal constituents of the marine environment, and some of them are essential to marine organisms, all metals are toxic above some threshold level. Mussels have proven to be useful for biomonitoring chemical contamination and, therefore, have been used for indicating levels of trace metal concentrations, in the marine environment. Moreover, mollusks are study organisms for their inclusion in the human diet.

The aim of this work was to determine the concentration of metals in the mussels (*M. galloprovincialis*) collected at 8 sites from Apulia coast, to investigate contamination level and public health risks associated with consuming mussels harvested from these areas. Moreover the goal of this study was also to estimate the weekly intake and compare it with the provisional tolerable weekly intake (PTWI) recommended by JECFA [1]. Metal concentrations were similar to those detected in other Italian coastal zones, and indicate that the seafood under investigation poses no hazard to human health because metal content is within the permissible range established for safe consumption by humans.

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ABC-PO-08 Zinc oxide (ZnO) oil pigment: chemical aspect of delaminating processes after drying

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Zinc oxide (ZnO) is a pigment today well commonly present in the oil paintings both alone and in mixture with titanium dioxide and lead carbonate. Although the use of this pigment is over all the world very common nevertheless some of its characteristics seem to represent a risk to the painted surface. In the literature, it is often reported that “Paints containing zinc oxide exhibit severe delaminating problems after drying” so much that fragility of the painted layer by this pigment results.

This phenomenon occurring expecially when the pigment is applied alone and brings to its loss. The reaction, probably of radicalic origin, has not yet been understood: the most supported hypothesis is that hydroxide and superoxide radicals start the reaction able to go on through the interaction among humidity, atmospheric oxygen and UV light, so producing the degradation of the oil binders.

The development of the reactions seems to largely depend on purity degree and particle dimensions. Particularly, as reported by Morgan [1-3] the particles of smaller dimensions seem to promote the formation of the “crequalure”. To assist this hypothesis, different commercial ZnO products (alone, not mixed with other products) were used as preparing layer on which another pigment layer was spread.

The pigments were examined both for their organic components and for inorganic ones in order to point out similarities and differences of composition and of behaviour in presence of other pigments.

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ABC-PO-09 Distribution of metals and PCB in deep-sea sediments of the Mediterranean Sea

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The Mediterranean Sea has been recognized as a marine region of special concern from the environmental point of view due to its particular hydrographical characteristics. It is a semi-enclosed basin with a negative water budget, where evaporation exceeds precipitation plus river runoff, which is compensated by a water inflow from the Atlantic Ocean through the Strait of Gibraltar. This feature has significant implications for the accumulation of contaminants from point and diffuse land based sources [1]. Most of the research on Mediterranean bottom sediments was performed in coastal areas [2-3], but data on metals and PCB in Mediterranean deep-sea cores is still lacking.

This study represents a systematic research performed on metals and PCBs determination in deep-sea cores sediments. The vertical profiles of metals in sediment were investigated in detail to elucidate the temporal behavior of metals. Sediment samples were collected with a box corer from ten sites during an oceanographic sampling campaign aboard the Italian research vessel Urania in July 2006 in the Eastern and Western basins of the Mediterranean.

As regards metal and PCB levels recorded in this study generally fall in the range of the lowest values available in the literature. Metal concentrations in sediment profiles were not uniform. In most cores the concentrations decreased from the surface and were within the range of values of the earth's crust.

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ABC-PO-10 Hydroxide nanoparticles for deacidification and concomitant inhibition of iron-gall ink corrosion of paper

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Historically valuable paper objects are rapidly deteriorating and their long-term conservation requires a full understanding of the chemical degradation mechanisms to conceive appropriate methodologies for conservation. The main cellulose degradation pathways are the acid hydrolysis of glycosidic bonds and oxidation. Low pH values can lead to cellulose depolymerization even at room temperature [1]. Ancient manuscripts were usually executed by using iron-gall-inks. These were obtained by reaction of iron (II) sulfate (i.e. *vitriol,* as reported in old recipes) with tannins extracted from gall-nuts, to give a pyrogallate complex of iron (III) and sulfuric acid [2]. However, acid-catalyzed hydrolysis of cellulose is not the only paper degradation pathway due to the presence of iron-gall ink. In fact, transition metal ions usually catalyze cellulose oxidation through a free radical mechanism, which produces hydrogen peroxide *in situ* [3].

This paper reports an investigation on the use of magnesium hydroxide nanoparticles dispersed in alcohols to inhibit two different and synergistic degradation processes usually affecting historically valuable manuscripts and common paper documents. We show that the preservation of paper from acid hydrolysis and oxidative ink corrosion can be achieved by stabilizing the final pH of deacidified paper around 6.5-7.5. PH control may allow to reduce the catalytic action of metals and minimize radical production. The inhibiting action of magnesium hydroxide nanoparticles are compared to magnesium oxide particles present in one of the best mass deacidification method (Bookkeeper) [4].

Note: This work has been partly supported by the project *TemArt*; *Programma Operativo Regionale - Regione Toscana*, co-financed by *Fondo Europeo di Sviluppo Regionale* (*POR CreO FESR 2007-2013*).

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ABC-PO-11 Application of multivariate statistical methods for the classification of the Apulian region ground waters.

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Multivariate statistical techniques such as Discriminant Function Analysis, Cluster Analysis, Principal Component Analysis, Absolute Principal Component Score and Neural Networks have been applied to data set formed by 895 samples and 15 parameters divided among four provinces of Apulia region (Bari, Lecce, Foggia, Taranto). The data set used has been obtained in the frame of the project "Expansion of regional agro-meteorological network" (2004-2007) funded by Apulia Region. Within the project 473 wells were monitored in order to assess, monitor and manage of regional groundwater quality.

Principal Component Analysis and Absolute Principal Component Analysis allowed to identify, for each province, the sites diverging from the mean cluster; while Discriminant Function Analysis pointed out the effective division among waters quality of different provinces.

Province	1	2	3	4	Total	correct %
1	181,6686	21,5539	11,29014	9,237385	223,75	81,19%
2	16,35096	172,1154	18,93269	16,35096	223,75	76,92%
3	2,712121	2,712121	174,9318	43,39394	223,75	78,18%
4	15,98214	15,09425	49,72222	142,9514	223,75	63,89%
Total	216,7138	211,4757	254,8769	211,9337	895	75,05%

Tab.1 Confusion matrix on dataset considered: 1 denotes Foggia Province, 2 Bari, 3 Lecce and 4 Taranto Province.

In Table 1 the confusion matrix obtained through leave one out cross validation method is shown. Results show a correct percentage of classification equal to 75%.

Variables whit high discriminatory power among groups, individuated by Wilks' lambda, are shown in table 2; they are: Ca^{2+}, NO_3^-, Na^+, Cl^-, Electrical Conductivity. In the further investigations a neural network model will be applied in order to improve the correct classification.

Var	Wilks □□	Partial Wilks□□□
pH	0.377256	0.648061
Elect Cond	**0.252416**	0.968579
Ca^{++}	**0.251305**	0.972862
Mg^{++}	0.311180	0.785672
K^+	0.268803	0.909532
Cl^-	**0.257734**	0.948595
NO_3^-	**0.251545**	0.971934
SO_4^{2-}	0.270020	0.905434
HCO_3^-	0.289341	0.844971

Tab. 2 Variables selected by Wilks' lambda

ABC-PO-12 Nanoparticles for the Consolidation of Lecce Stone

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Nanotechnology provides new concepts and materials for the conservation of cultural heritage items. In particular, innovative products based on nanometric particles of different compounds have been proposed in recent years for the conservation of stone materials. In the present study the consolidation effectiveness of some inorganic nanoparticles dispersions (silica, calcium hydroxide and strontium hydroxide) are evaluated and compared to that exhibited by tetraethoxysilane.

$Ca(OH)_2$ and $Sr(OH)_2$ nanoparticles [1, 2] have been prepared and characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), fourier transform infrared spectroscopy (FTIR) and micro raman spectroscopy. The dispersions stability of both $Ca(OH)_2$ and $Sr(OH)_2$ nanoparticles in water as well as in propan-2-ol has also been determined by UV-vis spectrophotometry. Moreover, the process of the nanolime carbonatation has been examined using FTIR and micro raman spectroscopy.

Aqueous dispersions of the considered nanoparticles have been applied to standard specimens of Lecce Stone, a highly porous biocalcarenite. Other specimens of the same stone have been treated by tetraethoxysilane (white spirit solution), used as a reference.

The effects of treatment on the stone surface have been studied by water capillary absorption and permeability to water vapour tests as well as by colorimetric measurements and optical microscopy observations. Distribution of the applied product into the stone has been examined by porosimetry measurements and SEM-EDX experiments.

The resistance to salt crystallization of the treated specimens has been evaluated by performing the dry weight loss (DWL) test. [3]

All the results obtained after treatment by the considered nanoparticles and tetraethoxysilane will be compared each other and discussed.

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ABC-PO-13 Carbonaceous nanoparticle molecular inception from radical addition and van der Waals coagulation of polycyclic aromatic hydrocarbon systems. A theoretical study.

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Carbon nanoparticles, [1] generated during combustion at relatively low [O_2] or under pyrolysis conditions, can be seen both as soot precursors and as primary pollutants in themselves. Soot particle inception, with transition of relatively low-mass molecular systems from the gaseous phase to a solid nature through coagulation/condensation, is believed to take place via chemical reactions as well as van der Waals (vdW) interactions involving polycyclic aromatic hydrocarbons (PAHs) or derivatives[2]. Here, radical addition between open and closed shell molecular PAH-like systems is examined by density functional theory, and different σ bond formations are compared with the previously discussed stacking of the aromatic components[3]. Energetic and entropic effects are examined. At higher T, formation of aliphatic bridges (hence reticulation) appears to be of the utmost importance to link PAH-like moieties, with a preference for more extended arrangements (due to entropic effects). More packed structures, promoted by vdW interactions (an energetic effect), may be favored by lower T. Thus, when the gas in the flame cools down, reticulation could be followed by inter- or intramolecular stacking. These distinct processes can take place within different T ranges, but are not mutually exclusive: in particular, σ bond formation helps subsequent stacking, since crystallites would be more easily produced at lower T by stacking of already bound elements. Therefore, the mechanistic picture offered by the calculations bears out a structural model for carbonaceous particle growth in which an initial more amorphous core, generated at higher T through successive radical attacks and σ bond formations (hence reticulation involving growing adducts), can subsequently become enclosed in an external shell which grows at a lower-T regime and presents more ordered zones[4]. It cannot be excluded that limited transitions from amorphous zones to more ordered zones could take place within internal regions of the particle, provided the local texture of these regions were sufficiently sparse to allow “extended to packed arrangement” rotations in the adducts.

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ABC-PO-14 Preliminary studies of paint samples by ToF-SIMS technique

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In this work we present preliminary results obtained by Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS) of paint cross sections collected from different parts of a Sienese painting. The aim of this study is to identify both the pigments and the binders present in the painting cross sections and their distribution within the different pictorial layers in order to define the state of conservation of the painting and the pictorial technique used by the artist. The presence of proteinaceous binders (rabbit glue and/or casein) suggests the use of tempera technique. Cholesterol is not detected, so we can exclude the use of the egg binder. The preparatory layer is composed by gypsum and proteinaceous binders, i.e. rabbit glue and/or casein. Cinnabar and white lead are also identified.

The ToF-SIMS results will be discussed and compared with those obtained by means of other well established techniques in painting studies, such as Scanning Electron Microscopy-Energy Dispersive x-ray Spectroscopy (SEM-EDS), Fourier Transform Infra Red (FTIR) spectroscopy and Gas Chromatography-Mass Spectrometry (GC-MS).

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ABC-PO-15 The Roman wall paintings at Pompeii: archaeometrical investigation of preparatory drawings (*sinopie*) and pigments.

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The archaeological site of Pompeii is a unique heritage of architecture, sculpture, paintings and mosaics. The wall decorations that adorn the *domus* and *villae*, constitute the most extraordinary aspect of the site, not only for the variety of styles but also for the refined pictorial technique used. The definition of the chemical nature of the pigments and binders used in Pompeii, results in an abundance of information on the origin, on the workshop production, on the technical knowledge of workers and lines of communication and marketing of painting shops that operated on the site. There are several studies that were conducted to learn about materials and production techniques used at that time [1] and different hypotheses have been advanced such as the use of encaustic, fresco, tempera or more elaborate methods [2] [3]. These hypotheses were tested on more than fifty samples taken from the wall paintings of seven different buildings of the famous archaeological site. In particular, this study concerned two major research areas, such as identification of the materials used for the fabrication of preparatory drawings (*sinopie*) and reconstruction of the palette and painting techniques used and, to this aim, a multi analytical approach, comprising optical, chromatographic and spectroscopic methods, was used. In the present communication the relevant results will be reported.

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ABC-PO-16 A reconstruction of the living space in a community of Early Bronze Age in Sicily: results of a multidisciplinary study.

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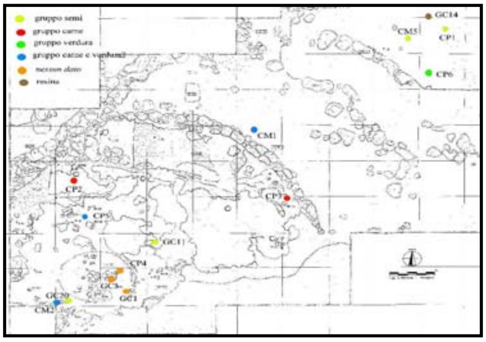
The main aim of this paper is to trace the use and the organization of space in a prehistoric human groups. The purpose, therefore, is to reconstruct the living space of this community, as produced by the interaction between the physical space and the actions and activities which took place within it. Both archaeological and chemical analyses seemed appropriate to carry out the study aimed at understanding the actual use of the vessels and linking the vessel function with the use of space finding as well. In the past, in fact, certain activities could take place outdoors or in specific areas inside the hut. The aim was to trace the connection among the type of food consumed, the shape of the used vessel, the sort of activity and space in which it took place. The case study is the Sicilian Early Bronze Age (2200-1450 b.C.) hill site of Santa Febronia. The village of Santa Febronia was discovered in 1995 [1]. At the top of the hill the remains of a hut of 4.80 m in diameter were found; the hut was destroyed by a fire; a large quantity of artefacts in their original functional position has been found. The study consisted in two steps. The objects distribution, mainly pottery, respect to the space and the structure has permitted to distinguish the storage areas from the ones destined to preparation and consumption of food. The chemical residue analysis in search of absorbed lipid and protein [2] has been used to identify the connection between the food processed and the space. The study revealed the multifunctionality of both space and pottery and confirmed the distinction of storage areas from the others. Moreover, it permitted to distinguish an area probably dedicated to storage of water.



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ABC-PO-17 Application of HPLC-HR-TOF-MS to the Analysis of Natural Pigments and Dyes in Cultural Heritage Artefacts

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The identification of complex mixtures such as lakes applied to paintings is an analytical challenge in cultural heritage studies because of many factors, such as the matrix intrinsic chemical complexity, the availability of very small fragments of pictorial film and the low thickness of the organic pigments layer usually employed for the realization of glazes and shading effects.

In this work we present the application of High Liquid Chromatography coupled with High Resolution Time of Flight Mass Spectrometry (HPLC-HR-ToF-MS) to the characterization of organic pigments traditionally employed by artists from antiquity to the first decades of XX century. The main goal is the development of an innovative approach to be used for routine analysis of natural substances present in cultural heritage artworks.

Only the combination of efficient chromatographic separation procedures coupled with the high mass resolution of the employed spectrometer allows to obtain the selectivity and sensitivity required for such characterization activity.

The planned approach involves three steps: 1) the extraction and preparation of lakes starting from natural (seeds, leaves, roots, berries, bark, flowers, insects, etc.) raw materials prepared according to selected original traditional recipes found in ancient treatises, such as the *Bolognese Manuscript*, the *De Arte Illuminandi*, and the *Il libro dell'arte of Cennino Cennini*; 2) the development of specific HPLC-MS methods for the analysis of the above mentioned pigments, also after artificial aging processes; 3) the validation of the developed methods by application to real samples collected from paintings of various ages and origins.

Concurrently, a detailed characterization of lakes by spectroscopic tecniques (e.g. FTIR, UV-Visible Spectrophotometry) will be carried out resulting in the creation of a complete reference spectra database.

Here we present the state of the art and the obtained results so far obtained.

ABC-PO-18 Extracts from Karité nuts reveal an ambivalent resource against termite pests

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Termites (Isoptera) are among the worse insect pests for wooden structures and their presence may represent a serious threat for cultural heritage, especially in those areas where climate and environmental conditions are favourable to these insects.The Old Continent is increasingly jeopardized by the obnoxious assaults of these insects, due to the high density of housing, to the haphazard urbanization and globalization, to the novel ecological patterns in use in the bio-masonry and to the antique remnant of mansions and sacred architecture.

Presently, sustainable management of termite pests includes the use of preventative measures (eg. application of repellents/antifeedants) and the use of baits with slow-acting termiticides.

The nuts of *Butyrospermum parkii* (Sapotaceae), tree native to West-Central Africa, are used to produce shea (karité) butter, welcome in the manufacture of cosmetics and food stuff. Aborigens believe that the residue from shea-butter extraction is capable to protect their houses from termites, which are extremely abundant in these regions (1). To verify if these popular beliefs have scientific basis, experiments were performed with European subterranean and drywood termites, respectively *Reticulitermes lucifugus* (Rhinotermitidae) and *Kalotermes flavicollis* (Kalotermitidae). Therefore an hydroglyceric extract of shea nut shells (the only pericarp) and an acqueous extract of shea cake (obtained from de-husked ground kernels, and thus phase oil-free) were used in short-term choice-tests and in long-term force-feeding trials, in order to assess the feeding deterrence or stimulation.. The results show that for both termite species shea cake extract is a feeding deterrent, thus confirming its potential as a wood preservative. However, most interestingly, the extract from shea nut shells elicited a very strong feeding stimulant effect, which looks extremely promising to increase the attractiveness -and therefore efficiency- of the baits.

Further analytical investigations (to determine the total rate of terpenoids and polyphenols) on both extracts are in progress in order to identify the active components responsible for the observed effects.

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ABC-PO-19 Changes in Sediment Heavy Metals Contamination and Bathymetry in The Lagoon of Venice over the Last Two decades

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The Lagoon of Venice is a transitional ecosystem, on the Northwestern coast of the Adriatic Sea, covering a 550 km^2 wide area, whose depth is shallower than 2 m for its 75%. It is connected to the sea through three inlets which regularly exchange water and sediments during the tidal cycles. Over the past millennium, the Lagoon has been modeled by both natural and human factors. Man activities, which included some engineering works, commercial shipping, dredging of channels, severe and in many cases illegal clam harvesting, have strongly modified the natural structure of channels, salt-marshes and bottom. Moreover, the central lagoon area has been affected by an heavy pollution from the industrial zone of Porto Marghera, atmospheric fall-out of pollutants and drainage of contaminants from the mainland.

This study has examined the trend of sediment heavy metals pollution in the central part of the Lagoon over the last 25 years (1987–2010) in relation to the changes in bathymetry. Five sediment sampling campaigns were carried out in 1987, 1993, 1998, 2003 and 2010 and the levels of some heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb) were analyzed with ICP-OES after microwave acid digestion [1]. A number of articles have monitored the pollution extent of the lagoon and the deposition/erosion processes and pointed out some changes in the existing legislation, which imposed stricter limits to waste discharges [2,3] . Variations in bathymetry were calculated from the data of two campaigns (1970s and 2000s) carried out by the Servizio Informativo del Magistrato alle Acque di Venezia [2]. Bathymetry variations evidenced moderate erosion in the largest part of the lagoon with the exception of some border sectors where a moderate sediment accumulation was recorded. Chemical results showed a progressive evident decrease in contamination from 1987 to 2010 for all the analyzed elements.

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ABC-PO-20 Analysis of perchlorate in Italian drinking waters

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Perchlorate (ClO_4^-) is used as an oxidant in rocket fuel, missiles, flares and fireworks [1] and is persistent in the environment due to its high solubility in aqueous media. It has been detected in matrices associated with human exposures, including drinking water and food [2]. Exposure to perchlorate is of concern, due to the compound's ability to reduce the uptake of iodide by the thyroid gland and, subsequently, the production of the thyroid hormones thyroxin (T4) and triiodothyronine (T3) [3]. In 1998 perchlorate was added to the U.S.EPA Contaminant Candidate List and many states adopted their own drinking water standards to limit its health impact [4]. The analysis of perchlorate is usually performed by ion chromatography with conductivity detection [5]. Since detection by conductivity is not specific to perchlorate but responds to any species with sufficient specific conductivity, the IC method does not provide absolute evidence for the presence of perchlorate. To improve the specificity of detection, EPA method 331.0 used ion chromatography electrospray ionization tandem mass spectrometry (IC-ESI-MS/MS) for the determination of perchlorate ion in drinking water with a detection limit of 0.022 µg/L [6].

Prior to our study, there was no documentation of the occurrence of perchlorate in Italian waters. In this study, concentrations of perchlorate were determined in sixty two drinking water samples collected from different Italian regions. A rapid, accurate and sensitive reversed-phase LC-ESI-MS/MS method was used for the determination of trace level perchlorate. Pre-treatment of samples using silver and barium cartridges (Dionex) was used to remove chloride and sulphate anions. Perchlorate was detected in more than 70% of the analysed samples with concentration ranging from 5 to 74.8 ng/L. The lowest level detected belongs to water samples from Calabria, whereas the highest concentration belongs to Basilicata region.

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ABC-PO-21 Adsorption and Competitive Adsorption of organic compound mixtures on zeolites

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Groundwater pollution by organic compound mixtures is an actual problem because of their noxious effects on human health and ecosystem. Volatile aromatics, toluene, chlorinate compounds, dichloroethane, and oxygenates, (tert butyl methyl ether MTBE), have been received worldwide attention due to theirs widespread contamination of surface water [1].

The conventional process of polluted water treatment was found to be obviously insufficient with the improvement of water quality demands; thus it is needed to develop more efficient, economic and convenient water treatment technology.

Considerable attention have been paid to adsorption technologies as efficient and versatile methods for water treatment.

Zeolites are a class of molecular sieves that have a well-defined micropore dimensions and composition in a rigid crystal lattice. These materials are stable at high temperature and have good adsorption capacity [2].

In this work, adsorptions of dichloroethane, MTBE and toluene on different hydrophobic zeolites, faujasite (FAU) and MFI (ZSM5) were studied. Both adsorption equilibrium and the adsorption kinetics of organic compounds in water solution were investigated. The experiments were carried out for single-component as well as mixtures of the compounds in order to investigate adsorption competition. The interactions between zeolite and organic compounds were furthermore investigated by thermogravimetric and structural analysis.

Favourable adsorption kinetics along with effective adsorption of organic compounds into zeolite pores make this environmentally-friendly material a tool with interesting applications for the removal of organic contaminants from wastewater [3].

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ABC-PO-22 Atmospheric corrosion of quaternary bronzes: 1-year field exposure to an urban marine environment

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This work is part of a long-term project, aimed at investigating the correlation between environmental parameters and corrosion of different alloys, used for artistic purposes, in an urban marine atmosphere.

Since June 2010, a metal/environment monitoring station is active in the sea-town of Rimini, where specimens of the quaternary bronze G85-5-5-5 and weathering steel are exposed in sheltered and unsheltered conditions.

Weight variations, colour changes and patina evolution are periodically monitored. As far as the specimens exposed in unsheltered condition, the release of the alloying metals is monthly evaluated by analysing the leaching rain, collected through racks suitably designed. At the same time, microclimatic parameters (temperature, relative humidity, wind direction and intensity, solar radiation) and concentration of main pollutants (NO_x, O_3, PM_{10}) are daily recorded; bulk depositions are monthly collected and analysed for main soluble ions and trace metals. Data from specimens and environmental monitoring are compared and correlated.

Results obtained for the quaternary bronze during one year of exposure are presented.

ABC-PO-23 Evaluation of the ultrafine particle concentration at different sites of the Veneto Region

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Particulate matter has been recognized as one of the most important air pollutants, and recently the health and environmental implications associated with atmospheric nanoparticles have prompted considerable research activities [1]. In the framework of the RESMIA project, founded by the Regione del Veneto, an intensive monitoring campaign of the ultrafine fraction of the aerosol is in progress; the aim of the study is to evaluate the spatial and temporal variability of the ultrafine particle distribution at seven sites of the Veneto Region where the impact of the human activities is different, by considering both the particle number and the mass concentration.

Some preliminary results show that the median number particle concentration (> 4 nm) at the background site is about 3 times lower than the particle concentration found at the traffic site; however at both stations a clear circadian variability appears, as shown in figure 1 and previously reported in literature [2].

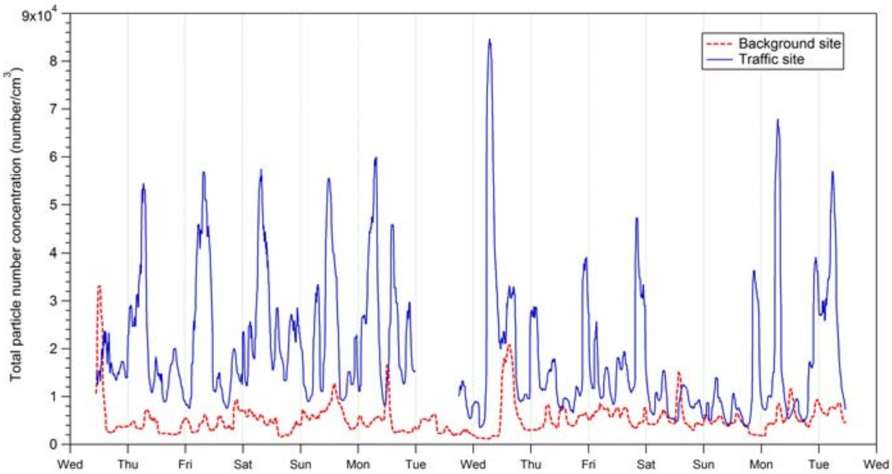

Figure 1. Temporal (smoothed) trends of number particle concentration at background and urban sites.

[1] P. Kuma, A. Robins, S. Vardoulakis, and Rex Britter, *Atmospheric Environment*, 44, **2010**, 5035-5052.

[2] F. Wang, F. Costabileb, H. Li, D. Fang, and I. Alligrini, *Atmospheric Research*, 98, **2010**, 69–77.

ABC-PO-24 Extraction of BTEX from diffusive samplers

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The use of CS_2 in the extraction of volatile organic compounds (VOCs), when sampled in the atmospheric ambient by means of active or passive devices filled with activated charcoal, is by far a standardized procedure. However, due to the highly hazardous nature of CS_2 a challenge to the research community has been to find alternative non-toxic solvents or mixture, or at least with a lower level of toxicity. Few years ago Bertoni et al. proposed a comparative study were dichloromethane, a less dangerous and unpleasant solvent, was used in comparison to carbon disulphide. Their results highlighted that CH_2Cl_2 is useful in the extraction of aromatics molecules but the recovery factor was lower than that of CS_2 , in most cases in the order of 60%. In this study we report the results obtained by different extraction pathways using several solvents, selected among the most common solvents usually present in a chemical laboratory, for their low boiling point and high TLV-TWA value. Each solvent was used following the standard procedure by immersing the exposed charcoal for 60 min, followed by gaschromatografic analysis. Moreover, in each case, as an alternative procedure the use of a mini Soxhlet extractor was introduced which allows several extraction cycles, depending upon the extraction time. The Soxhlet apparatus was appositely realized for the treatment of extremely low volume of solvent. As it is shown in Figure1, the entire amount of BTEX adsorbed by charcoal was recovered after only few cycles of extraction by using dichloromethane as a solvent.

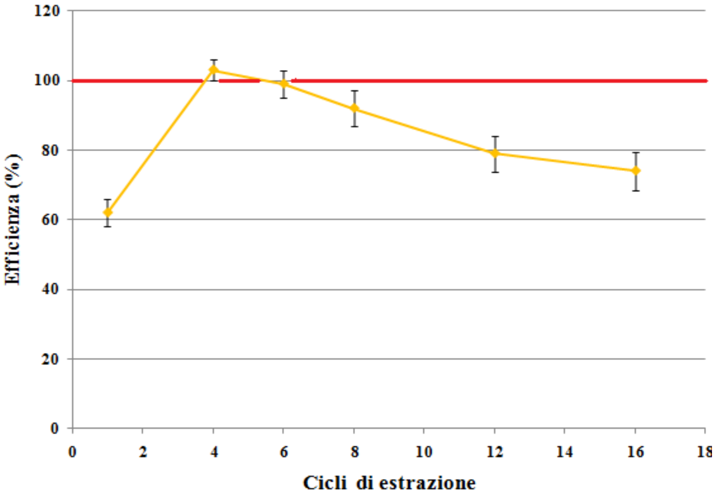

Figure 1. Extraction of BTEX from activated charcoal by CH_2Cl_2 in Soxhlet apparatus. The red line refers to 100% recovery performed by the usual CS_2 extraction procedure.

ABC-PO-25 Thermodynamics-based orientors for holistic interpretation of ecosystem services.

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Ecosystems can be viewed as thermodynamic systems, open to energy and matter, that self-organize towards higher complexity and organization of matter, create order, and self-maintain far from thermodynamic equilibrium [1]. Ecosystems also produce goods and services that are beneficial for human society and economy.

In order to detect ecosystem properties and dynamics in this context, some relationships can be acknowledged among the input supporting them, work capacity and useful output. These relationships can be represented by thermodynamics-based orientors e.g. emergy and eco-exergy, and the concept of ecosystem services. In particular, the ratio of eco-exergy to emergy flow is an indicator of efficiency in transforming the basic solar energy available into the structure of an ecosystem [2]; the ratio of eco-exergy to ecosystem services represents the annual work capacity increase of an ecosystem as a measure of all the possible services it can offer (not only the services that anthropic systems actually utilize), and can be compared with the actual flow of services utilized [3]; the ratio of the value of the ecosystem services to the emergy flow that supports the system can be considered as a measure of the ability of the ecosystem to use inputs and provide services [4].

A 3D diagram is introduced to present the inflows of resources, measured in terms of solar emergy, on the x axis, the work capacity embodied in the system biota, expressed in terms of eco-exergy, on the y axis, and the useful services for humans, valuable in economic terms, on the z axis. This multi-dimensional holistic approach makes clear that inputs are used up, directly or indirectly, to produce services in output and/or to develop the system, and enables to have an indication of changes in ecosystem dynamics, structure, services. Within this framework, a thermodynamic/socio-ecological evolutionary time path is proposed: from young system, to climax-stage system, to socio-ecological integrated system.

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ABC-PO-26 Biomonitoring of trace metals and organic compounds along the Apulian Coasts (Southern Italy) using *Mytilus galloprovincialis*.

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The present work reports the final results from a biota monitoring program, during the years 2008-2009. This project is mainly targeted toward the monitoring of the coastal water quality, using mussels as bioindicators, and the identification of contamination spatial trends. Mussels were sampled in 26 stations located along the marine coastal and transitional waters of the Apulian region, including both south-western Adriatic and Ionian areas. The analyzed contaminants were: heavy metals, chlorinated pesticides, chlorinated solvents, organophosphate pesticides, polychlorinated biphenyls, polybrominated diphenyl ethers (PBDEs), alkylphenols, polycyclic aromatic hydrocarbons and organotin compounds. Results were also compared with the National and International Regulations. Concerning metals, the maximum concentration of mercury (0.8 mg/kg d.w.) was found at the mouth of Saccione River (Station MC1A), in the Adriatic Sea, while Pb and Cd levels where found to be maximum in stations MC5A – Capoiale Mouth (3.3 mg/kg d.w) and AT7 - Varano Lake (2.5 mg/kg d.w.) respectively. For these three metals, no mollusks collected in any station exceeded the legal limits set by EU Regulation n. 1881/2006 (0.5 mg/kg w.w. for Hg, 1.5 mg/kg w.w. for Pb and 1.0 mg/kg w.w. for Cd). Concentrations of total PAHs (Σ PAHs) ranged from not detectable to 287.4 μg/kg d.w. (VM71A – mouth of Galeso River, Mar Piccolo of Taranto). Also in the station VM70A, Mar Grande (Ionian Sea) was observed high concentration of total PAHs (205.7 μg/kg d.w.). It is worth to mention that in the station VM71A, naphthalene represents about 73% of the total PAH concentrations. No stations exceeded the EU limit (EU Regulation 1881/2006) of 10.0 μg/kg w.w. for benzo[a]pyrene in bivalve mollusks. This compound represents a “contamination target” for carcinogen PAH pollution. The sum of PCB congeners ranged from not detectable to 383.8 μg/kg d.w. near the mouth of Galeso River (station VM71A), Mar Piccolo of Taranto, Ionian Sea.

Concerning chlorinated pesticides, only 4,4’ DDE was found with the maximum concentration in the Mar Piccolo (second inlet) and near the mouth of Ofanto River (26.9 and 18.7 μg kg^{-1} d.w. respectively).

In these situations, frequent controls are needed in order to safeguard marine ecosystem and human health due to the consumption of seafood.

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ABC-PO-27 A preliminary study on the influences of paper components on the degradation of cellulose

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Archival holdings are strongly subjected to degradation due to the materials they are made and, to be able to intervene effectively, the knowledge of the causes and mechanisms behind the processes of degradation of cellulose in these artefacts is required. [1,2] In addition, the interventions have to be differentiated according to the specific "pathologies" of each item.

Paper is a complex system made up of several components interacting each other, such as cellulose, sizing, inks, coatings, and so on. Most of the articles on paper degradation currently reported in the literature refer to the simple degradation of cellulose, which clearly represents its main component, but certainly not the only one. The aim of the study presented in this communication is the study of the interactions between the different components of the paper and how these interactions influence the mechanisms and the rate of polymer degradation.

Among all considered variables, particular attention will be given to iron gall ink for the importance played as a writing material from the middle ages until the 20th century. Its relevance in paper conservation is also related to the so-called phenomenon of *corrosion* that can be observed in many ancient documents. *Corrosion* occurs with noticeable paper degradation and can even results in perforations or losses of material. [3]

The project involves the development and the optimization of different methods of artificial aging in order to balance the main degradation mechanisms of paper, hydrolysis and oxidation. [4] Data obtained from simulated samples will be compared with those from original documents to evaluate the effectiveness of the methodologies applied in simulating aging.

Both ancient and modern papers are considered and compared in the present work, to verify if the changes in the historical manufacture have introduced or replaced components affecting the rate of degradation of the artefacts.

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ABC-PO-28 Protection of Lecce Stone by fluorinated polymers

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Lecce Stone represents a very challenging substrate to protect, due to its characteristics, most of all its porosity and pore size distribution.

Different products have been proposed as suitable to protect this substrate, acting as efficient hydrophobic barrier, thus preventing condensed water uptake by capillary absorption, which represents one of the main causes of degradation of the material.

In the present work some commercially available fluorinated polymers (i.e. a fluoroelastomer [1], a fluorinated polyurethane [2] and a perfluoropolyether derivative) have been applied as hydrophobic agents to Lecce Stone. They have been used as received and after proper modifications (for instance a chemical cross-linking or an addition of little amount of filler).

As the performance of a treatment may depend not only on the applied product and on the stone characteristics, but also on the procedures used for its application [3], different treatment procedures were considered.

The effectiveness of each treatments was evaluated by water capillary absorption and water vapour permeability tests as well as by color variation and contact angle measurements.

Different instrumental techniques such as micro ATR-FTIR and SEM-EDS were also used for surface and cross-section characterization of the stone specimens, in order to investigate the distribution of the protective materials after the treatment.

This work has shown that fluorinated polymers may be considered effective protecting agents for Lecce Stone, but their performance can be strongly affected by treatment procedures. For instance the considered fluoroelastomer afford a satisfactory protection from water when the formation of a film on the stone surface is allowed, while the effectiveness of the perfluoropolyether derivative is not affected by the application method.

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