



Strasbourg (France)

E-MRS 2005 Spring Meeting  
May 31 – June 3, 2005

## **SYMPOSIUM Q**

### **Materials science and cultural heritage**

Symposium Organizers :

**Yannis Chryssoulakis**, Ormylia, Greece

**Marie-Claude Corbeil**, Canadian Conservation Institute, Canada

**Michel Menu**, C2RMF, Louvre, Paris, France

**Giuseppina Padeletti**, CNR – ISMN, Monterotondo (Roma), Italy

**Michael Stuke**, MPI, Goettingen, Germany

Papers to be published in Applied Physics A

# E-MRS 2005 Spring Meeting

## SYMPOSIUM Q

Tuesday, May 31, 2005  
Mardi 31 mai 2005

Morning  
Matin

9:00

**WELCOME**  
by the Symposium Organizers

### Session I : Metals

Session chair : **M. Stuke**

**Q-I.01** 9:20 -Invited-

#### LARGE SCALE INVESTIGATION OF CORROSION MECHANISMS OF BRONZE ARCHEOLOGICAL ARTEFACTS FROM MEDITERRANEAN BASIN

G.M. Ingo, T. De Caro, ISMN-CNR, CP 10, 00016 Monterotondo Stazione, Rome, Italy, A. Çilingiroglu, Ege University, Bornova-Izmir, Turkey, **E. Angelini**, Politecnico di Torino, Torino, Italy, P. Vassiliou, National Technical University of Athens, Greece, M. Gener, CENIM-CSIC, Avda. Gregorio del Amo n° 8, 28040 Madrid, Spain, V. Gouda, NRC, El-Tahir Street Dokki 12622, Cairo, Egypt, W. El-Saddik, The Egyptian Museum, Maydan El Tahir Square, Cairo, Egypt, Z. Al-Saad, Yarmouk University, PO Box 566 University Street, 211-63 Irbid, Jordan, S. Khosroff, Institute National du Patrimoine, 2000 Le Bardo, Tunisia, L. Bousselmi, INRST, B.P. 95, 2050 Hammam Lif (Tunisia), O.M. Al-Jarrah, Jordan University of Science and Technology, PO Box 3030, Irbid 22110, Jordan, Z. Madjoub, Université Djillali Liabes, BP 89, 22000 Sidi-Bel-Abbes, Algeria

In the framework of the EFESTUS project financially supported by the European Commission (INCOMED contract No. ICA3-CT-2002-10030) and aimed to find tailored strategies for the conservation and restoration of archaeological value bronze artefacts from Mediterranean Countries, well-defined groups of Cu-based alloys archaeological objects selected as a function of the archaeological context, of the degradation state and of the expected chemical composition and structure, have been studied via a large number of different analytical techniques such as SEM-EDS, XRD, OM, GDOES, XPS, ICP-MS, AAS, DTA-TG, XRF, FTIR and XPS. It is worth noting that the manufacturing period of the selected artefacts varies from about 2400 BC to 1000 AD (a time range of 3400 years) and consider the most important civilisations of the ancient Mediterranean Basin including Egyptians, Greeks, Carthaginians and Romans and further, that the selected archaeological artefacts have been produced by using the main ancient manufacturing techniques employed to produce bronze artefacts. Their chemical composition is very wide and includes all kinds of the ancient Cu-base alloys such as copper, low tin and high tin also leaded materials. This innovative approach has been utilised in order to gain further insight into the micro-chemical structure of the stratified corrosion layers and of the bulk metallurgical features to be used for identifying the corrosion mechanisms and then, the best conservation procedures.

**Q-I.02** 10:00

#### CHARACTERISATION OF SILVER AND GOLD GILT SILVER WIRES FROM FIVE "KISWA", EMBROIDERED SILK KAABA COVERS PRESENTLY EXHIBITED AT THE TOPKAPI PALACE MUSEUM, DATED BETWEEN 16TH AND 19TH CENTURIES

Ali Fuat Çakir(a), Gülsu Simsek(a) and Hülya Tezcan(b), (a)Istanbul Technical University, Department of Metallurgy and Materials Engineering, Istanbul, Turkey, (b)Curator of Textiles, Topkapi Palace Museum, Istanbul, Turkey

The silk cloths known as Kiswa, valuable and revered silk cloths embroidered with silver and gold gilt silver threads, are used to cover Kaaba, the holy place of pilgrimage in Mecca for Muslims. Ottomans exercised sovereignty over Kaaba between 1517 and 1918 and Sultans had sent various Kiswa to Kaaba. Physical and chemical characterisation of five different silver and gilt silver wires obtained from five different Kiswa sent to Kaaba between the 16th and the 19th centuries and presently exhibited at the Topkapı Museum in Istanbul, are the subject of this investigation. Characterisations are carried out both by conventional metallographic techniques as well as modern analytical instruments such as Scanning Electron Microscope, Field Emission Gun and Energy Dispersive Spectroscopy and FEG equipped with Electron Beam Selected Diffraction unit. The chemical and physical composition of the wires and their coatings, and also identification of corrosion products are determined and the technique of coating preparation was evaluated and compared.

**Q-I.03** 10:20

#### UNCOMMON CORROSION PHENOMENA OF ARCHAEOLOGICAL BRONZE ALLOYS

T. de Caro, G.M. Ingo, ISMN-CNR, CP 10, 00016 Monterotondo Stazione, Rome, Italy

In the framework of the EFESTUS project financially supported by the European Commission (INCOMED contract No. ICA3-CT-2002-10030) the investigation into the structure of many archaeological bronze artefacts has been carried out by means of the combined use of X-ray photoelectron spectroscopy (XPS), scanning electron microscopy combined with energy dispersive spectrometry (SEM-EDS), X-ray diffraction (XRD) and optical microscopy (OM) techniques. The results have provided good insight into the corrosion layers evidencing in some bronze Roman coins the occurrence of some uncommon corrosion phenomena that give rise to the formation of a green complex chlorine-phosphate of lead (pyromorphite) as well as a copper depletion from the outermost corrosion layers. Furthermore, the results have evidenced that some Cu-based Roman republican coins with a surface gold-like appearance are coated by a thin and smooth layer of a complex iron and copper sulphide (chalcopyrite) adherent very closely to the surface of the coins. It is worth noting that the copper-iron sulphide is the primary corrosion product because it was not formed later from the alteration of basic copper carbonates or sulphates. These results show that the coins were likely accidentally placed in an anaerobic and humus rich soil and the chalcopyrite layer has been produced via the interaction of the iron of the soil, the copper of the coin and the sulphur produced by the decomposition of organic matter in an almost oxygen free environment.

The above described surface enrichments of P, Cl, S and Fe show a strict relationship between some soil constituents and corrosion products thus evidencing the importance of the study of the archaeological context also from a minero-chemical point of view.

10:40

**BREAK**

### **Session II : Organic materials**

**Session chair : M.R. Schilling**

**Q-II.01** 11:00

#### JAPANESE LACQUER: AN INTEGRATED RESEARCH & COLLABORATIVE CONSERVATION PROJECT

Brenda Keneghan, Conservation Department, Victoria & Albert Museum, London SW7 2RL, U.K., Ricky Wildman, School of Mechanical and Manufacturing Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, U.K.

The Mazarin Chest is renowned as one of the finest pieces of Japanese export lacquer to have survived from the late 1630's, and is a star object in the V&A's collection. At present the chest is not stable enough for display or transport and is at some risk of further loss even if it simply remains in storage. In the West, the conservation treatment of lacquer objects is usually based on the principle of reversibility, whilst Japanese conservators generally utilise traditional urushi-based materials and techniques that are non-reversible but maintain cultural continuity. In this project selected ageing characteristics and mechanical and water sorption properties are investigated in order to assess potential future effects of the use of traditional Japanese lacquer conservation materials and techniques. It is also proposed to compare selected mechanical properties of some traditional Japanese and Western synthetic consolidants used in lacquer conservation treatments. Facsimiles of lacquer coatings have been made and are being artificially aged to produce micro-cracking similar to that found on the surface of the Mazarin chest. They shall be treated in a traditional Japanese manner and the effects of further ageing and relative humidity fluctuations monitored, to establish whether this treatment consolidates and strengthens a photo-degraded lacquer surface or damages it by causing additional strain. The techniques being used in this project include FTIR spectroscopy, SEM, speckle interferometry, and various mechanical measurement techniques.

Research work on the project has just commenced and the authors would welcome ideas and discussion.

**Q-II.02** 11:20

#### PERMANENCE AND DURABILITY OF DIGITAL PRINTS ON PAPER

Marjeta Cernic, Leopold Scheicher, Jozica Dolenc, Pulp and Paper Institute Ljubljana, Bogisiceva 8, POB 1728, 1000 Ljubljana, Slovenia

Ever more spread use of different unconventional digital printing systems pretending optimal cooperation between printers and papermakers, producers of coating and printing colour and surface and protection agents to made the requirements for the quality of each other to achieve the best printing quality as well as the application of the final product. Graphic products are often exposed to negative influence of external climate condition. Surface treatment with lamination and varnishing of the final product is a common solution. In the frame of the application research work with cooperation of the printing industry we researched permanence and durability by artificial ageing paper, image of prints and final printed product. We researched the influence of artificial ageing of nonprinting and printing paper in electro photographic printing technique (Xeikon), with the two kinds of surface treatment on the quality of the printed products. The results of the basic and surface properties characteristics, mechanical strength, optical and colorimetric characteristics of paper as well as the evaluation of the permanence upon EN/ISO 9706 (&#260;) have shown unsuitable optical and colorimetric properties of paper and prints. Those characteristics carried on the poor optical stability and colour image printing. We have stated the great instability on colour prints - changes of colour and contrast and the colour equilibrium are destroyed. The ageing resistance of surface treatment with different varnishes has showed very bad results, too. The results of research work are very useful for evaluation of durable printing paper quality by using various new digital printing systems and for evaluation of printing material with permanent value.

**Q-II.03** 11:40

**FTIR IN SITU TRANSMISSION STUDIES ON THE KINETICS OF PAPER DEGRADATION VIA HYDROLYTIC AND OXIDATIVE REACTION PATHS**

J. Lojewska(a), H. Lubanska(b), T. Lojewski(a), (a)Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland, (b)Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Kraków, Poland

Millions of books worldwide are threatened by paper disintegration that proceeds through the cleavage of glycosidic bonds in cellulose caused by both hydrolysis and oxidation and catalysed by aluminium sulphate. Today, the rescue effort is on mass deacidification of those books which have not been completely damaged. The aim of this study is the preparation of a spectroscopic experimental basis for modelling of the kinetics of paper degradation involving mixed-control mechanism.

This has been achieved using an in situ FTIR transmission technique. In order to discriminate between two reactions model paper samples were aged under various conditions (pure water vapour, dried air, 100, 150°C). The focus was on the spectra between 1500-1900 cm<sup>-1</sup>, where various carbonyl groups appear as the products of paper ageing. The elaborated procedure of spectra standardization allowed correlating the bands area with conversion of cellulose upon ageing. From the time evolution of the bands the overall kinetic curves were generated and analysed. The positions of the carbonyl bands were verified by independent experiments. Basing on these facts a mechanism assuming parallel-consecutive oxidation and autocatalytic hydrolysis was proposed.

12:00

**LUNCH**

Tuesday, May 31, 2005  
Mardi 31 mai 2005

Afternoon  
Après-midi

### Session III : Instrumental and conservation methods

Session chair : E. Angelini

Q-III.01 13:30 -Invited-

#### STUDY AND CONSERVATION OF ARTWORKS BY EUROPEAN TRANSNATIONAL ACCESS TO ADVANCED FACILITIES

**B. Brunetti**, INSTM and SMAArt, Dipartimento di Chimica dell Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

Relevant applications of material science to art and archaeology involve European Transnational Access services to advanced facilities. These include synchrotrons or neutron sources, but also other specific facilities such as MOLAB (Mobile Laboratory) or AGLAE (Accelérateur Grand Louvre d'Analyse Elementaire).

In archaeology, an interesting example is the synchrotron study on origin and nature of the lustre decoration technique in Medieval pottery. Lustre consists of a high-density distribution of silver and copper nanoclusters within the glaze and has been recently studied by EXAFS at the beamline GILDA-BM08 in Grenoble. The manufacturing technique corresponds to a silver and copper ion-exchange with the alkali of the glaze, followed by reduction at 600°C. The technique is substantially identical to that used today to synthesise glass-metal nanocomposites. The recently available Transnational Accesses to MOLAB and AGLAE have shown great potentialities. MOLAB (Mobile Laboratory) consists of a unique collection of portable equipments, belonging to four joint Italian institutions (SMAArt-Perugia, OPD-Firenze, CNR-ICVBC-Firenze, and INOA-Firenze), available to carry out non-destructive measurements in-situ, i.e. in a museum room, in a church, etc.. The pool of MOLAB equipment is composed by ten portable instrumental devices, such as scanning IR-colour reflectograph, a laser micro-profilometer, a compact micro-Raman, a fiber optic FT-IR, and others. Starting from 2004, MOLAB equipments have made possible to carry out in-situ non-destructive studies of precious immovable artworks, such as paintings of Perugino and Raphael, or of relevant sculptures, such as the David of Michelangelo

Q-III.02 14:10

#### LASER SPECTRAL ANALYSIS OF SURFACE LAYERS AS APPLIED TO AUTHENTICATION OF PAINTINGS

E.V. Klyachkovskaya, V.A. Rozantsev, S.V. Gaponenko, E.A. Ershov-Pavlov, Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus, 70, F. Skaryna Avenue, 220072 Minsk, Belarus and N.M. Kozhukh National Art Museum of Belarus, 20, Lenin Street, 220030 Minsk, Belarus

The final objective of the study is to create a new technology of examining and authentication of paintings based on laser breakdown spectroscopy (LIBS) use. At the present stage, LIBS technique has been developed for elemental analysis of surface layers of solids. The analysis includes on-surface and in-depth profiling of the layer composition. The technique allows determining distributions of chosen elements along specimen surface and in the bulk of material using emission spectra of the laser-induced plasma. For this, conditions were found to record the spectra from a single laser shot. Also, the laser parameters were chosen to obtain regular laser craters of known depth and diameters. The technique has been tested and optimized at analysis of pre-prepared layers with known compositions. Among them diamond-like layers on silicon wafers, as well as painting samples were used. The latter consisted of canvas covered with ground and several selected paint layers. Finally, the technique has been applied for the analysis of some original paintings from Portrait Gallery of Nesvizh (Belarus). The results show good prospects of the LIBS as applied to paintings authentication.

The study was realized using laser elemental micro-analyser specially designed for surface analysis. The device includes Nd:YAG Q-switched double pulse laser, microscope, video monitor, PC-controlled moving sample table and CCD record system.

**Q-III.03** 14:30**FEMTOSECOND LASER FILAMENTS ENABLE REMOTE LIBS ANALYSIS WITH POTENTIAL APPLICATIONS IN THE MONITORING OF SCULPTURE AND MONUMENTS**

D. Anglos(a), D. Gray(a) and S. Tzortzakis(b), (a)Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), 711 10 Heraklion, Crete, Greece, (b)Laboratoire pour l'Utilisation des Lasers Intenses (LULI), Ecole Polytechnique, 91128 Palaiseau, France

Even though most applications of laser-induced breakdown spectroscopy (LIBS) utilize nanosecond lasers, the use of short pulses is gaining ground particularly because it provides certain advantages related to both fundamental studies and delicate analytical problems. Among them an advantage unique to ultra-short laser pulses is the formation of filaments that effectively enable the controlled delivery of high laser intensities at long distances in air. The filamentation phenomenon opens new prospects for the use of ultra-short laser pulses for LIBS analysis at remote locations.

In this work is reported, for the first time, the use of filaments produced from ultraviolet sub-picosecond laser pulses (248 nm, 450 femtoseconds) for the remote analysis of test samples, related to objects of cultural heritage. Several metal samples such as brass, lead, aluminium or copper were clearly identified on the basis of their distinct emission lines in the recorded optical emission spectra. Studies regarding the formation and characterization of plasma induced by the UV femtosecond filaments and technical details related to remote signal collection are described. Clean LIBS spectra were collected at distances as long as 15 meters (limited by the dimensions of our laboratory) employing a simple telescope near the source. Advantages such as automatically controlled intensity deposition suggest that there is significant potential for utilizing UV femtosecond filaments for the remote analysis of sculpture and monuments.

**Q-III.04** 14:50**SPECTROSCOPIC ANALYSIS USING A HYBRID LIBS-RAMAN SYSTEM**

A. Giakoumaki and D. Anglos, Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), P.O. Box 1527, 711 10 Heraklion, Crete, Greece

In the present study, a novel laboratory system, combining two spectroscopic techniques, laser induced breakdown spectroscopy (LIBS) and Raman spectroscopy, for the analysis of materials in objects of cultural heritage, was developed. While both Raman microscopy and LIBS have been used extensively as diagnostic tools in art and archaeology their combined use is limited, as it generally requires different instruments. The goal of this research is to demonstrate the applicability of a hybrid LIBS-Raman unit as an analytical tool for the investigation of samples and objects related to cultural heritage.

The system proposed utilizes a nanosecond pulsed Nd:YAG laser (532 nm) for both LIBS and Raman analysis. In the Raman mode a low intensity beam probes the sample surface and the scattering signal is collected into a grating spectrograph coupled to an intensified CCD detector, which records the Raman spectrum. In the LIBS mode a single high intensity pulse from the laser irradiates the sample surface and the time- and spectrally-resolved emission from the resulting laser ablation plume yields the LIBS spectrum. The advantage of the hybrid system implemented, is that it employs a single laser source, common optics and the same spectrograph-detector system detection enabling the convenient application of both analytical techniques in a practically simultaneous way. The performance of the hybrid LIBS-Raman unit was tested with the analysis of selected pigment and mineral samples. Preliminary results from the use of the system to identify pigments in a real painting are also reported and the capabilities and limitations of the setup are discussed.

**Q-III.05** 15:10**AN INTEGRATED HIGH RESOLUTION AMS RADIOCARBON DATING AND ION BEAM ANALYSIS APPROACH FOR THE STUDY OF ARCHAEOLOGICAL CONTEXTS**

G. Quarta, K. Butalag, G. Demortier, M. D'Elia, L. Maruccio, L. Calcagnile, Centro di Datazione e Diagnostica, Department of Engineering of Innovation, University of Lecce, 73100 Lecce, Italy

The experimental potentialities of the CEDAD (Centro di Datazione e Diagnostica) AMS radiocarbon dating and Ion Beam Analysis facility of the University of Lecce, Italy have been recently enhanced by the installation of a new beam line dedicated to in vacuum and in air characterisation of objects of archaeological relevance. In the new beam line the proton probe beam is extracted in air through an Al window and the induced x-ray emission is detected by a Si(Li) and a Ge detectors. The performances of the AMS facility have been improved as well in terms of precision (0.2-0.3 % errors are routinely achieved), background and sample throughput (50 samples are prepared and measured per week). The possibility to use the same apparatus to perform both AMS radiocarbon analyses and IBA (PIXE and RBS) characterisations give unique possibilities in the study of archaeological contexts. We report on the compositional analyses performed in air on seven ceremonial golden artefacts of the Bronze Age found in Roca, Melendugno, Lecce. The analyses have shown that the objects are compositionally homogeneous between them and are likely formed by native gold with a concentration ranging from 83 to 89 % wt. With the aim to date the objects <sup>14</sup>C AMS (Accelerator Mass Spectrometry) analyses have been performed on short lived vegetable rests found in the same context in direct archaeological association with the golden artefacts. The temporal relationships between the selected samples, supposed on the base of the archaeological evidence, have been used as statistical constraints during the calibration of the conventional radiocarbon ages in order to reduce the calendar time range. By this approach the artefacts have been dated to 1270-1110 cal BC with a 2 sigma confidence level.

**Q-III.06** 15:30

**CONSERVATION OF ACID WATERLOGGED SHIPWRECKS:  
NANOTECHNOLOGIES FOR DEACIDIFICATION**

Rodrico Giorgi, David Chelazzi, Piero Baglioni, CSGI c/o Department of Chemistry, University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino (Florence), Italy

The study of waterlogged wooden artefacts, particularly ancient wrecks, is fundamental in the field of cultural heritage conservation. Samples, from the Swedish warship Vasa, are under investigations at the CSGI laboratories in order to develop innovative methods for its preservation.

Vasa represents a unique case in the study of ancient wrecks. The ship sank in his maiden voyage in 1628, and remained in the water of Stockholm harbour for 333 years. In 1961, it was recovered and treated for 17 years with polyethylene glycol, in order to prevent wood from shrinking after drying, which would otherwise bring to a dramatic loss in the physical and mechanical properties of the structure.

In the last 4 years the problem of the acidity of wood came out as a strong threat for its conservation. The production of sulphuric acid inside the wooden structure is actually the cause of a consistent chemical damage through the acid hydrolysis of cellulose, and a physical one, due to the crystallization of sulphate minerals in the wooden pores associated to consequent mechanical stresses.

The sulphates originate from a large amount of elemental sulphur, a product of the metabolic action of the bacteria in the wasted, anoxic water of the Stockholm harbour. The oxidation process of the elemental sulphur, started with the recover of the ship, is believed to produce of about five tonnes of sulphuric acid, besides the two already present in the wooden structure. Storage in anoxic water, thus, prevented attack from common fungi, rot and other wood degrading microorganisms, but set the basis for a dramatic degradation.

The task of our restoring intervention was, mainly, the neutralization of the wood acidity. Complete neutralization was achieved by application of nanoparticles of earth-alkaline carbonates and/or hydroxides. Such a treatment provides an alkaline reservoir inside the wood. Nanoparticles absorbed in the wood from an alcoholic dispersion adhere to the wooden fibres. They release hydroxyl ions leading to neutralization. This method was already effective in the deacidification of paper.

Oak and pine samples from the wreck were characterized and treated with alkaline non aqueous nanodispersions. Deacidification effect was monitored by pH changes and all the treated samples were submitted to artificial ageing in order to demonstrate the effectiveness of the method. Experiments showed excellent results and opened a new perspective in wood conservation.

Finally, this new method is environmentally clean and inexpensive.

**Q-III.07** 15:50

**IN SITU NON-DESTRUCTIVE IDENTIFICATION OF SURFACE MARBLE ALTERATIONS BY FIBER OPTIC MID-FTIR REFLECTANCE SPECTROSCOPY**

C. Ricci(a), C. Miliiani(b), L. Cartechini(b), A. Sgamellotti(b), and B.G. Brunetti(a), (a)INSTM and Centro SMAArt, Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy, (b)CNR-ISTM, Sezione di Perugia, c/o Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy

Main chemical alterations of marble monuments exposed to urban environment consist of contamination due deposition of sulphates, oxalates, nitrates, phosphates and chlorides, or to organic contamination generally related to past conservation treatments made by natural polymers -such as waxes and proteins- or synthesis products -such as siloxanes and acrylic resins.

It has been demonstrated, both by laboratory tests and in situ measurements on ancient relevant sculptures, that surface species on a marble substrate can be successfully identified by a fiber-optic portable equipment using mid-infrared reflectance spectroscopy. The measurements do not imply any sampling. Laboratory tests showed that the complex optical phenomena taking place by reflectance on layered sample can effectively lead to the identification of the surface alteration, even in the case where low alteration signals are overlapped to the strong absorbance of the carbonate substratum. Successful identification has been shown possible for sulphates, phosphates, oxalates, waxes, proteins, and resins. The technique has been applied in three different case studies of preventive conservation of indoor and outdoor sculptures: the Antelami's "Deposizione dalla Croce", conserved at the Parma's cathedral, the Giambologna's "Ratto delle Sabine" at the Loggia dei Lanzi in Firenze, and the Michelangelo's "David", conserved at the Galleria dell'Accademia in Firenze.

16:10

**BREAK**

16:30-18:30

**POSTER SESSION**

**POSTER SESSION**  
Tuesday, May 31, 2005  
16:30 – 18:30

Wednesday, June 1, 2005  
14:00 – 16:00

**Metals**

**P/Q.01**

**INTEGRATED APPROACH TO THE CHARACTERIZATION OF ARTIFACTS OF THE BRASILIAN COLONIAL PERIOD**

Emma Angelini, Sabrina Grassini, Politecnico di Torino, Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Torino, Italy, Guillermo Solorzano, Guadalupe do Nascimento Campos, Depto. de Ciência de Materiais e Metalurgia, PUC-Rio, Rio de Janeiro, Brasil

Several common-use artifacts (coins, faience, cult objects, etc..) coming from two excavations sites near Rio de Janeiro, two sugar farms Historico do Rochedo and Cruzeiro, and an old church Nossa Senhora da Conceicao dos Amorins- Aldeia Velha, have been object of this investigation, aimed to integrate the physicochemical characterizations with the identification of the degradation mechanisms and the proposal of restoration procedures, the last ones, in particular for metallic artifacts, through the study of accelerated ageing on reference materials. The microchemical, micromorphological and microstructural analysis have been designed in order to be comprehensive with minimal impact on the integrity of the artefacts; optical microscopy-OM, X-ray diffraction-XRD, X-ray fluorescence-XRF, scanning electron microscopy equipped with electron microprobe-SEM+EDS have been employed. A cleaning step followed by a consolidation step has been carried out on glassy artefacts, while on metallic artefacts the mechanical cleaning has been followed by a stabilization treatment when necessary. For long-term protection against aggressive agent, the deposition by PECVD of SiO<sub>x</sub>-like films has been proposed; the efficacy of these coatings has been tested on copper-based reference alloys of composition similar to the one of the artefacts.

**P/Q.02**

**BRONZE ROMAN MIRRORS : THE SECRET OF BRIGHTNESS**

G.M. Ingo(a), E. Angelini(b), T. de Caro(a), P. Plescia(a), and C. Riccucci(a), (a)ISMN-CNR, CP 10, 00016 Monterotondo Stazione, Rome, Italy, (b)Politecnico of Turin, Italy

In the framework of the EFESTUS project financially supported by the European Commission (INCOMED contract No. ICA3-CT-2002-10030) high tin leaded bronze Roman mirrors found during the archaeological excavation of the industrial-metallurgical area of the Phoenician-Punic-Roman city of Tharros (western Sardinia) have been studied by means of the combined use of X-ray photoelectron spectroscopy (XPS), scanning electron microscopy combined with energy dispersive spectrometry (SEM-EDS), X-ray diffraction (XRD) and optical microscopy (OM) techniques. The study of the surface microchemical structure of the Roman mirrors has allowed to understand the origin of their high chemical stability and appearance. Indeed, some areas of the selected Roman mirrors are still characterised by a reflecting surface even though they have been buried for 2000 years in the soil. The microchemical results obtained from these areas have revealed they were surface enriched with tin via the so called inverse-segregation phenomenon that is one of the most interesting and rarely used methods used in ancient times to coat the surface of metal artefacts for producing a silvered-like surface through the concentration of tin (or antimony or arsenic) on the surface during the blank casting. Indeed, the results indicate that the presence of tin was enhanced first during the blank production by tailoring the thermal parameters thus inducing the inverse segregation phenomenon and then, via intentional selective corrosion processes based on pickling solutions thus resulting in a surface enrichment of tin as well as in a copper depletion at the outer surfaces.

**P/Q.03**

**PRODUCTION OF REFERENCE "ANCIENT" Cu-BASED ALLOYS AND THEIR ACCELERATED DEGRADATION METHODS**

T. de Caro(a), G.M. Ingo(a), M.P. Casaletto(a), A. Çilingiroglu(b), P. Vassiliou(c), C. Samara(c), E. Angelini(d) and C. Riccucci(a), (a)ISMN-CNR, CP 10, 00016 Monterotondo Stazione, Rome (Italy), (b)Ege University, Bornova-Izmir, Turkey, (c)National Technical University of Athens, Greece, (d)Politecnico di Torino, Torino, Italy

In the framework of the EFESTUS project financially supported by the European Commission (INCOMED contract No. ICA3-CT-2002-10030) the chemical composition and metallurgical features of a large number of archaeological artifacts made by copper based alloys have been determined. Furthermore, the study of the corrosion products grown on the archaeological Cu-based artifacts have revealed that the quite ubiquitous and nearly constant presence of chlorine as main corroding agents. These information have been exploited to produce reference Cu-based alloys whose chemical composition and microchemical structure is similar to that of the ancient alloys and to propose the guidelines for carrying out the accelerated degradation tests to produce corroded samples for testing corrosion inhibiting products. The proposed tests were based on soil, chemical and chemical + soil induced degradation and the microchemical structure of the artificially produced corrosion layers have been compared to those present on archaeological artifacts. The comparison shows that the chemical + soil induced degradation produce patinas similar to those grown on archaeological artifacts from a chemical, structural and micromorphological point of views.

- P/Q.04** COMBINED USE OF SEM-EDS, XPS, XRD AND OM FOR THE CHARACTERIZATION OF THE CORROSION PRODUCTS OF SILVER ROMAN COINS  
G.M. Ingo(a), S. Balbi de Caro(b), T. de Caro(a) and C. Riccucci(a), (a)ISMN-CNR, CP 10, 00016 Monterotondo Stazione, Rome, Italy, (b)Soprintendenza per i Beni Archeologici dell'Abruzzo, Chieti, Italy  
In the framework of the PROMET project financially supported by the European Commission (INCOMED contract N° 509126) and aimed to develop new analytical techniques and materials for monitoring and protecting metal artefacts and monuments from Mediterranean region, the corrosion products grown on silver Roman coins found during archaeological excavations have been studied by means of the combined use of X-ray photoelectron spectroscopy (XPS), scanning electron microscopy combined with energy dispersive spectrometry (SEM-EDS), X-ray diffraction (XRD) and optical microscopy (OM) techniques.  
The results evidence that silver and copper i.e. the main alloying element, are corroded during the burial to form different chemical species such as silver chloride, cuprous oxide and copper basic carbonates. Furthermore, the results show that the above cited corrosion products form stratified structures and that the small copper islands scattered in the silver matrix give rise to the formation of paratacamite i.e. the so called bronze disease, that corrodes completely the copper globules. The results show that XRD and OM in combination with SEM-EDS have significant potential in studies of the corrosion products of archaeological silver objects for their stabilisation and conservation.
- P/Q.05** MICROCHEMICAL INVESTIGATION OF GREEK AND ROMAN SILVER AND GOLD PLATED COINS : COATING TECHNIQUES AND CORROSION MECHANISMS  
T. de Caro(a), G.M. Ingo(a), S. Balbi de Caro(b), I. Fragalà(c), G. Bultrini(c) and C. Riccucci(a), (a)ISMN-CNR, CP 10, 00016 Monterotondo Stazione, Rome, Italy, (b)Soprintendenza per i Beni Archeologici dell'Abruzzo, Chieti, Italy, (c)Università di Catania, Italy  
In the framework of the PROMET project financially supported by the European Commission (INCOMED contract N° 509126) and aimed to develop new analytical techniques and materials for monitoring and protecting metal artefacts and monuments from Mediterranean region, the metallurgical techniques used in ancient times for coating the copper core of coins with a thin or thick layer of gold or silver have been studied by means of the combined use of X-ray photoelectron spectroscopy (XPS), scanning electron microscopy combined with energy dispersive spectrometry (SEM-EDS), X-ray diffraction (XRD) and optical microscopy (OM) techniques.  
This innovative approach has been utilised in order to gain further insight into the micro-chemical structure of the external regions of the objects as well as of the bulk metallurgical features. The results indicate that several methods were used in ancient times by the craftsmen including the simple mechanical application of a thin malleable gold foil or the most complex and sophisticated method based on the use of mercury i.e. the so called fire gilding. Finally, the above cited analytical methods have been also used to investigate the corrosion mechanisms of the coins found during the archaeological excavations for identifying their degradation mechanisms.
- P/Q.06** NON-DESTRUCTIVE CHARACTERIZATION OF ALLOY COMPOSITION AND TEXTURAL PROPERTIES OF ETRUSCAN BRONZES: A METHODOLOGICAL STUDY  
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A combination of conventional analytical techniques, such as X-Ray Fluorescence (XRF) and Electron Probe Microanalysis (EPMA) with novel applications of neutron scattering were employed for the non-destructive characterization of 6th Century BC Etruscan bronze plates. Neutron scattering experiments were carried out at the ROTAX beam line of the ISIS pulsed spallation neutron source of the Rutherford Appleton Laboratory (UK).  
The bronze plates pertain to a princely chamber tomb discovered in 1812 in the Umbrian countryside. The excavation brought to light a considerable number of plates (thickness 0.2-0.4 cm, surface area 5-25 cm<sup>2</sup>) used to richly decorate one ceremonial carriage, two war chariots and some furniture. The analytical investigations were aimed at providing the necessary clues for the correct assignment of several fragments in order to recompose the original plates. The work illustrates how the different analytical and experimental techniques responded to the investigation needs. One outstanding result is the validation of the powerful capability of neutron diffraction to provide extensive non-destructive, high sensitivity bulk analysis for the characterization of bronze phases compositions, strain and texture analysis, with relatively minor limitations as to surface patina, shape and dimensions of the artifacts. The compositional results obtained by Rietveld refinement analysis of the diffraction profiles allowed for a thoroughly meaningful comparison among the finds, while strain and textural properties could be related to the ancient Etruscan manufacturing techniques.
- P/Q.07** CONSTANTINE EMPIRE COINS: STUDY OF PLATING TECHNIQUES  
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A series of 'folles', belonging to Constantine Emperor period, have been investigated in order to clarify techniques used to fabricate and to silver plate them. Surfaces and cross section analyses performed respectively by X-ray Photoelectron Spectroscopy (XPS) and by SEM EDX investigation allowed to determine elemental compositions as well as depth profile distributions of relevant elements. Archaeometric investigation were assisted by the simultaneous study of bronze models plated in laboratory through two different silvering procedures: silver-mercury alloy and red-ox reaction between bronze and silver chloride. Experimental evidences on folles coins excluded both the methods and pointed to surface segregation of silver probably obtained by heating silver-rich bronze alloys.

- P/Q.08** ON THE COMPARATIVE STUDY OF THREE SILVER COINS OF THE III<sup>RD</sup> CENTURY B.C. MINTED IN KORKYRA, DYRRACHION AND BY THE ILLYRIAN KING MONOUNIOS  
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Three different silver coins of the III<sup>rd</sup> century B.C. from Korkyra, Dyrrachion and the Illyrian King Monounios belonging to the Kreshpan hoard were studied using several destructive and non-destructive methods. These are optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray fluorescence (XRF). Furthermore, the density and the microhardness were determined.  
From this investigation it turned up that the microstructure of the three coins is different. The Monounios coin, which contains about 2.8% Cu, is composed by large Ag grains separated by small inclusions of the Ag-Cu eutectic mixture. The coin from Dyrrachion, which contains about 3.8% Cu, seems to have a similar structure. However the Korkyra coin is much different. It contains less than 0.5% Cu and it is characterized by a very large number of twins scattered in almost every grain of the cross-section. Furthermore, its microhardness is about 52 to 58 HV, while for the other coins it is above 110 HV. These differences could possibly indicate different minting methods. Probably the Monounios coin was hot struck, the Dyrrachion coin was cold struck and the Korkyra coin was cold struck and annealed.

## Organic materials

- P/Q.09** IDENTIFICATION STUDIES OF PREHISTORIC WATERLOGGED WOOD  
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In archaeology, wood is an organic material that rarely survives, but it supplies an environmental and anthropical cultural heritage. Archaeological woods (A-woods), partially preserved only in particular conditions, are often so degraded to require a suitable investigation to be identified. In the present work we have analysed, by Scanning Electron Microscopy (SEM), 22 modern woody (M-wood) species, appropriately chosen on the basis of pollen analysis made in lake-dwelling archaeological site of FiaVè-Carera (Trento province, Italy). We thus created a wide reference table of SEM images of M-woods to be compared with A-woody species. To avoid damage of M-wood sections (transversal, longitudinal radial and tangential) and to permit thorough analyses, well defined sample handlings have been established that include cutting, dry, and SEM preparation (by also using liquid nitrogen freezing). The so established M-wood collection was used to identify several A-wood samples obtained from FiaVè-Carera prehistoric woody finds. Most of the A-woods was so waterlogged that freeze drying was required to avoid woody structural collapse. Freeze dried A-samples have been prepared and analysed by SEM. The results were used to infer on environmental and anthropical history of the local region. SEM analysis in such a research activity was really important due to scarcity and small dimensions of degraded A-wood samples, by also permitting to make a choice between hardwood and softwood and often the genus.
- P/Q.10** MODERN POLYESTER COMPOSITE MATERIALS IN CONTEMPORARY ART  
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This paper describes the pilot project that was carried out in the conservation department of the EVTEK Institute of Art and Design and in Oulu City Art Museum. There are three dimensional art objects and parts of installations made of composite materials containing gypsum, glass fibre and two component polyester resins in the collections of Oulu City Art Museum. Even if composite materials are considered to be chemically resistant, the artefacts made of polyester composites have started to undergo deterioration processes. This was definitely the case in part of the installation by Jan-Erik Andersson. This artefact was exhibited in the open air. The aim of this pilot project was to study the cause of deterioration in composite materials containing polyester. Ageing and degradation tests and analyses were employed to reveal the effect of unsaturated polyesters in the degradation process. To determine the composition and colour changes of tested materials, samples were analysed before and after ageing using FTIR (Fourier Transform Infrared Spectroscopy) microscopy, DRIFTS (Diffuse Reflection Spectroscopy), DSC (Differential Scanning Calorimeter) and CIE L\*a\*b\* colour measurements. The results of these references were also compared to the analytical data of the composite material artefacts. Analyses proved that there are clear differences in ageing properties and stability of different unsaturated polyester products. The pilot study also provided useful information both for preventive conservation and for conservation treatments of objects made of composite materials.
- P/Q.11** Py/GC/MS TECHNIQUE APPLIED TO THE STUDY OF IRON GALL INKS  
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This work presents preliminary measurements performed by pyrolysis capillary gas chromatography coupled with mass spectrometry on iron gall ink, iron gall inks on papers (PY/GC/MS). Ink preparation based on medieval recipes and study of their characteristics. The Department of Restoration and Conservation of Mesrob Mashtots Institute of Ancient Manuscripts, Matenadaran, Yerevan, Armenia are reading recipes from manuscripts and the Department of Book and Paper Conservation of the University of Applied Sciences and Art of Hildesheim, Germany is preparing solutions of inks then writing on pure cellulose paper Whatman N°1/ Cat N° 1001 185 by quill, brush, calamus. Recipes for the inks used in the manuscripts are to be found within the texts themselves. These recipes represent a valuable source of information. The aim of the research is to understand the composition similarities and differences between the Armenian inks and the inks so far researched by PY/GC/MS technique .

## Instrumental and conservation methods

### P/Q.12 POTENTIALITIES OF PORTABLE INSTRUMENTS FOR THE CHARACTERIZATION OF TANGIBLE METALLIC CULTURAL HERITAGE

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The studies performed in EFESTUS project supported by the European Commission (Contract N°: ICA3-CT-2002-10030) and aimed to develop tailored strategies for conservation, restoration and valorization of historical and archaeological copper-based artefacts from Mediterranean Countries, are a good example of the noticeable potentialities of some analytical portable instruments in the characterization of metallic artefacts.

The selected artefacts have been submitted to microchemical, micromorphological and microstructural analysis with different techniques (optical microscopy-OM, X-ray diffraction-XRD, X-ray fluorescence-XRF, scanning electron microscopy equipped with electron microprobe-SEM+EDS, glow discharge optical emission spectroscopy-GDOES, electrochemical impedance spectroscopy-EIS) in dependence of their dimension, typology, sampling possibility, easiness of temporary export, in order to elaborate the modellization of degradation processes before and after the excavation, to establish accelerated ageing procedures and to find proper conservation methods. Interesting results have been obtained with portable instruments properly developed with three of these techniques, (EIS, XRD, XRF). On Cu-based artefacts as coins, mirrors, arms and other common use objects, information about the stratified corrosion layers nature and about the bulk metallurgical features have been collected by means of XRD and XRF portable instruments and the protective effectiveness of natural patinas and/or of protective treatments has been evaluated with an EIS portable instrument. The satisfactory comparison of the experimental results obtained with portable equipments with the ones given by laboratory instrumentation confirm the potentialities of the employed portable instruments.

### P/Q.13 LASER CLEANING OF TEXTILES

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In order to analyse ancient textiles to identify the fibre, a good cleaning of the sample is necessary. The anaerobic environment (i.e. the peatery), aiding the preservation of such handmade textiles, often impregnates the textiles in such a way that the usual chemical procedures for cleaning are not sufficient while making the sample brittle. The use of laser pulses may offer an alternative method of cleaning. Four different textiles (wool, silk, flax, and cotton) have been investigated: after a series of preliminary cleaning experiments on untreated samples, consolidated samples, samples exposed to a lacustrine environment, and samples both exposed and consolidated have been irradiated with excimer laser pulses. Several combinations of the main laser parameters (energy density and number of pulses) have been tried in order to find the best irradiation conditions. A wide use of Scanning Electron Microscopy (SEM) has been made to analyze the induced morphological changes. The obtained results are well reproducible while proving the very high efficiency in material removal of the laser pulses: in the four investigated textiles, the laser cleaning procedure permitted the identification of the fibres.

### P/Q.14 EVALUATION OF THE PROTECTIVE EFFICACY OF SYNTHETIC ORGANIC COATINGS APPLIED ON STONE MONUMENTS

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Protection of stone materials from natural and environmental disintegration is an important step in the preservation of historical stone monuments and buildings.

The performance of five synthetic coatings for the protection of monuments of the Hellenistic and Byzantine period has been evaluated. The selected coatings included four commercially available siloxane- (Rhodorsil 224, Wacker 290) siloxane/acrylic- (Bayer LF) and perfluoroether-based compositions (Akeogard P) as well as a newly synthesized fluoro-organosilane (Ftorsam-39). Coatings were applied onto five well characterized and petrologically different stone substrates, such as two types of marble, a travertine, a sandstone and a newly baked brick compatible with Roman period bricks, used for the restoration processes in Galerius Palace, (Thessaloniki, Greece). The selected stone substrates are typical for the Southeast Mediterranean cultural heritage and are also used for the construction and decoration of contemporary buildings. The coatings' protective efficiency was investigated by measuring the water-stone equilibrium contact angle, water vapor permeability and water capillary absorption, according to the Normal Protocol. The measured parameters were integrated in a newly derived evaluation parameter, named Total Protective Efficiency (T.P.E.), which was used to rate the coatings on the basis of their protection ability. Rhodorsil 224 found to exhibit superior T.P.E. for three of the tested stones. Wacker 290 provided best T.P.E. when applied on brick and Akeogard P proved to be suitable for a particular type of marble. Finally, coatings were ranked with respect to their effect on the aesthetic appearance and optical properties of the tested substrates.

**P/Q.15****LASER CLEANING ON ANCIENT PARCHMENT**

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Laser cleaning is a technique used both in conservation and restoration of historical and cultural artefacts.

In several cases, this technique has been proved an attractive method for removing contaminants from critical surfaces. It has been found especially effective in removing sub micron particles or organic films and has found applications in several fields. In this work, we apply this technique to an ancient parchment dating from 1600. More precisely this parchment has been artificially dirtied with synthetic powder of graphite of 1-2  $\mu\text{m}$ . A number of tests of laser cleaning using Q-switched Nd:YAG laser treatment at different wavelengths (532 nm and 1064 nm) have been performed on parchment. A well working set of cleaning parameters, beam radius, fluence, repetition rate etc. has been found. Application of the "verso laser cleaning" technique is in course. In the usual laser cleaning the laser pulses are projected onto the sample surface to be cleaned, in the verso laser cleaning the pulsed laser beam impinges on rear sample surface. Good results were obtained using verso laser technique on textile fibers: while recto laser cleaning shows a damage to ink marks depending on pigment color, no damage is observed in "verso" laser cleaning. Different characterisation techniques have been employed to verify the cleaning and the possible damages determined by laser. In particular, micro X-Ray fluorescence (mXRF) provided information on the chemical composition, Scanning Electron Microscopy (SEM) was employed to examine the morphology, X-Ray microdiffraction (mXRD), GIXRD (Glancing Angle X-Ray Diffraction), microraman and infrared (IR) spectroscopies was used to detected the phases.

**P/Q.16****SURFACE LASER TREATMENT OF ANCIENT CALCITE: THE CASE OF THE GRAVE IN TORRICELLI (NAPLES)**

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Laser cleaning allows removing contaminations and encrustations from surfaces of different kind of materials without physical or chemical changes of the original surface. This technique has been effectively employed in many areas and recently it has a huge development in art restoration.

Its use has been considered to clean a 4th century BC chamber gravesite in Torricelle, near Nola (Naples). The wall painting could not be seen owing to bioorganic surface layer and resinous material originated from surrounding pinewood. In order to evaluate the technique effectiveness we studied the interaction of the light from a Q-switched Nd: YAG (pulse duration: 5 ns) equipped with SHG to work at wavelength of 532 nm. Several characterisation techniques have been employed to study the laser effect on the cleaning of the surface versus the operating parameters configuration. In particular, micro X-Ray fluorescence (microXRF) provided information on the chemical composition of the clean surface, Scanning Electron Microscopy (SEM) was employed to examine the morphology, X-Ray microdiffraction (microXRD), micro Raman and infrared (IR) spectroscopies were used to detect the phases. These techniques resulted to be effective in assessing the quality of the cleaning process. Moreover, the possible influence of the laser on the aragonite-calcite transformation has also been investigated and discussed.

**P/Q.17****RESTRAIN OF BIOLOGICAL ACTIVITY OF ULOCLADIUM SP SPORES IN ARTIFACTS WITH 157 NM LASER**

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High resolution AFM images of ulocladium sp spores reveal restrain of biological activity following laser illumination at 157 nm. Laser light dissociates the external multilayered proteinacious shell of the spores reducing thus their thickness up to the point where the high pressure of the nucleus destroys them by explosion. Thus the use of 157 nm lasers is an effective and controllable method for stopping biological activity of ulocladium sp spores in artifacts. This finding supports previous results of using 157 nm lasers against foxing in historic paper preservation [1].

1. Nanometric size control and treatment of historic paper manuscript and prints with laser light at 157 nm. Z. Kollia, E. Sarantopoulou, A. C. Cefalas, S. Kobe, Z. Samardžija. Appl. Phys. A 79,379, 2004 (2004).

**P/Q.18****STUDY ON IMPACT OF LASER IRRADIATION OF THE ARTIFICIALLY PATINATED BRONZE**

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The main objective of the research was to identify the effect of parameters of laser irradiation (wavelength and fluence) on the chemical composition and ageing of patinated bronze. The chemical composition and roughness of the surface layer were measured using FIB-SIMS system and white light interferometry, respectively. The laser used in the experiments was a Q-switched Nd: YAG with wavelength of 1064nm and 532nm and fluence varying from 0.5 Jcm<sup>-2</sup> to 1.5 Jcm<sup>-2</sup>. It was found that irradiation with fluence below damage threshold (0.5 Jcm<sup>-2</sup>) dramatically reduces concentration of industrial pollutants such as sulphur and chlorine on the surface of artificial patina. However it was found that even low fluence irradiation leads to the significant increase in C/Cu and O/Cu ratios during first 14 days after irradiation. The whitelight interferometry shows decrease or no alteration in thickness of patina layer. On the basis of obtained data there is a strong evidence that during a laser radiation top upper layer of artificial patina is destroyed and immediate oxidation process takes place resulting in more uniform oxide layer.

- P/Q.19** USE OF MID-INFRARED FIBER-OPTIC REFLECTANCE SPECTROSCOPY TO DETERMINE EFFICACY OF MICRO-EMULSION CLEANING AGENTS IN FRESCO CONSERVATION  
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Mid-Infrared Fiber-Optic Reflectance Spectroscopy (Mid-IR FORS), a sensitive, non-invasive technique for determining chemicals present on a surface, has been used for the first time to test efficacy of oil-in-water emulsions in restoring painted surfaces (in this case, removing an undesired varnish).  
The experiments were carried out by coating frosted glass slides with six common polymer varnishes (natural dammar, mastic, vinavil, acrylic resins) at three different concentrations. Spectra of the samples were collected by microreflectance single-beam infrared spectroscopy and fiber-optic reflectance infrared spectroscopy. Sharp, strong peaks specific to the varnish type (of wavelength ranging from 1715-1760) were discernable for (most) samples at all concentrations. Polyamine based gels were applied to remove varnishes from glass slides. Spectra were again collected using the same infrared reflectance techniques to determine if clearance of the "undesired" varnish was achieved.  
Results thus far indicate effective determination of efficacy by Mid-IR FORS analysis. The experiment is currently being repeated again on painted plaster supports, a condition which closer mimics an actual fresco painting.

## Paintings

- P/Q.20** BLACKENING PROCESS OF A XV CENTURY ITALIAN PAINTING: A XAFS STUDY  
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The investigation of the blackening process of ancient paintings is particularly interesting to improve both conservation and restoration procedures. The use of structural techniques being able to investigate both the surface blackened layer and the bulk part of the painting (not damaged by aging) is essential for this kind of study. In particular, the x-ray absorption spectroscopy provides exclusive structural information in a non-destructive way, so that it is very suitable for the cultural heritage field. While the measure of the x-ray absorption spectrum by means of the fluorescence yield takes contribution from both the blackened layer and the bulk part of the painting, the same measurement performed in the total electron yield mode allow to probe only the first 150 nm of the surface. In this work the XAFS measurements at Cu K-edge on fragments of a N. Liberatore painting (XV century) were carried out in both fluorescence and total electron yield mode. The aim of this study is to understand the blackening process of the pigments on the surface, considering fragments of different colour (blue and two kinds of green). The prevalence of oxidized copper phase has been observed, comparing experimental spectra with suitable standards (malachite, azurite, resinate, metallic copper and copper oxides). The near-edge structures and the whole XAFS spectra showed differences between the samples. Similarities have been found between a standard of azurite and a blue sample and between a standard of malachite and an altered green sample for fluorescence spectra. Moreover, for the two pigments, the differences between the XAFS spectra recorded in fluorescence and electron detection mode will be discussed.

## Stone, glass, ceramics

- P/Q.21** MINERO-PETROGRAPHIC, THERMAL AND MICROCHEMICAL INVESTIGATION OF HISTORICAL MORTARS USED IN CATANIA (SICILY) DURING THE XVII CENTURY AD  
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The combination of X-ray diffraction (XRD), scanning electron microscopy + energy dispersive spectrometry (SEM + EDS), differential thermal analysis-thermogravimetry (DTA-TG) and optical microscopy (OM) has been used to study several different ancient mortar samples taken from the S. Nicola Church (built after the devastating earthquake of the 1693) and other historic buildings located in Catania (Eastern Sicily). The investigation has been focused on the identification of the raw materials used to produce the different mortars and of their provenance as well as on relevant aspects of manufacturing processes. The minero-petrographic results have often shown that local volcanic raw materials have been used as aggregate fractions and in particular the new volcanic material (the ghiara) had been largely used for the construction of the walls of the monuments after the earthquake. The ghiara material was the product of the impressive Etna eruption of the 1669 that devastated Catania. The following reaction with the soil gave a layer of this typical ochre-coloured material. Furthermore, in order to precisely locate the ghiara provenance, geological surveys of the most important historic quarries has been also carried out and the results have allowed to identify the exploited sources of ghiara.

**P/Q.22****GLANCING-INCIDENCE X-RAY DIFFRACTION STUDY OF Ag AND Cu NANOPARTICLES IN GOLD AND RED LUSTRE DECORATION OF ITALIAN RENAISSANCE POTTERY**

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Lustre is one of the most important decorative techniques of Medieval and Renaissance pottery of the Mediterranean basin, characterized by brilliant gold and red metallic reflections.

Previous studies by various techniques (SEM and TEM, UV-vis, XRF, Rutherford back-scattering and EXAFS) demonstrated that lustre consists of an heterogeneous metal-glass composite film, formed by Cu and Ag nanoparticles dispersed within the outer layer of a tin-opacified lead glaze.[1-3] In the present work a preliminary investigation of original gold and red lustre samples from Deruta and Orvieto (two of the most important Italian centres of lustre Renaissance production) by means of Glancing-Incidence X-ray Diffraction (GIXD) technique has been performed. The study was aimed to provide information on structure and depth distribution of Ag and Cu nanoparticles, avoiding any sample preparation. Exploiting the capability of controlling X-ray penetration in the glaze, by changing the X-ray incidence angle in the range of 0,1o -5o, GIXD measurements allowed us to non-destructively characterize the crystalline phases present in the first micro&#61485;meters of the glaze. Diffraction patterns of Ag and Cu metallic phases have been observed, respectively in gold and red (copperlike) lustres. A comparison with the results obtained for samples of homogeneous flatness at different X-ray incidence angles provides an estimation of the nanoparticle depth distribution.

[1] J. Pérez Arantegui et al., J. Am. Ceramic Soc. 84 (2001) 442;

[2] I.Borgia et al., Appl. Surf. Science 185 (2002) 206;

[3] S. Padovani et al., Appl. Phys A, 79 (2004) 229.

**P/Q.23****CHARACTERISATION AND REPRODUCTION OF YELLOW PIGMENTS USED IN CENTRAL ITALY FOR DECORATING CERAMICS DURING RENAISSANCE**

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The present study is focused on both the characterisation of yellow pigments used during the Renaissance period in Italy and their reproduction according the ancient recipes. Indeed, the combination of different analytical techniques, namely the X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) has provided deep insights on a large number of yellow decorative layers present on Sicilian ceramic artefacts dated from 13th to the 19th century. Moreover their main chemical, structural and minero-petrografic features has been identified. The results have been compared both with literature data concerning the chemical composition of yellow decorations of Renaissance ceramics manufactured in central Italy and with data obtained from the study of yellow pigments produced according to the ancient recipes described by Cipriano Piccolpasso in "I Tre Libri dell'Arte del Vasaio" and by using the same ingredients available in ancient times. It is worth noting that these latter materials represent the typical yellow colorants used by the craftsmen of several important ceramic production sites in central Italy (Città di Castello, Urbino and Castel Durante) during the 16th century.

The results have evidenced some interesting differences between the yellow pigments obtained via the Piccolpasso recipes and those produced in Sicily thus demonstrating a limited technological transfer in the different production sites of ancient Italy.

**P/Q.24****STUDY OF BLUE COLOR IN ANCIENT MOSAIC TESSERAE BY MEANS OF LUMINESCENCE AND REFLECTANCE MEASUREMENTS**

A. Galli(a), M. Martini(a), C. Montanari(a), G. Poldi(b), E. Sibillia(a), (a) INFN and Dipartimento di scienza dei materiali, Università di Milano Bicocca, Via R. Cozzi 53, 20125 Milano Italy, (b)Istituto di fisica generale applicata, Università di Milano, Via Celoria 16, 20133 Milano Italy

A series of experiments on visible reflectance bands and on the thermoluminescence signal from glass matrix of blue ancient mosaic tesserae have been carried out. The results presented show the relationship between the nature of the glass matrix and the absorption band of cobalt chromophore ion. Thermoluminescence measurements with the evaluation of the electron trap depth characterize the color centers in the glass network. These two techniques have been applied to the identification of some optical properties of cobalt ion in the vitreous matrix.

**P/Q.25****PHOTOLUMINESCENCE EMISSIONS OF CERAMICS: A MARKER OF PRODUCTION TECHNOLOGY**

A. Galli, M. Martini, C. Montanari, E. Sibillia, INFN and Dipartimento di scienza dei materiali, Università di Milano Bicocca, Via R. Cozzi 53, 20125 Milano, Italy

Photoluminescence measurements have been performed on different sets of ceramic shards. In this work the results obtained from the ceramic body of lustred renaissance majolica shards produced in central Italy, as well as on others from hispano-moresque period, and from different production sites are reported. Analyzing the emission spectra obtained from all the samples involved in our study the emission bands can be attributed mainly to peaks assigned to alpha quartz and diopside. The results are discussed by taking into account also the XRD measurements. Considering some emissions present only in the PL spectra of lustre-decorated ceramics we can affirm that the PL measurements are able to supply a discriminating parameter.

14:00-16:00 **POSTER SESSION (continued)**

16:00 **BREAK**

**Session IV : Cultural heritage materials (joint session with symposium O)**  
**Session chair : M. Menu**

**Q-IV.01** 16:20 -Invited-

**APPLICATIONS OF SYNCHROTRON RADIOATION TO ARCHAEOOMETRY**

**Mario Vendrell**, Dept. Crystallography and Mineralogy, University of Barcelona, Spain  
From the very beginning, the scientific equipments also improved their accuracy while the amount of sample need were reduced in size and/or weight. This open a wide range of opportunities to the research of ancient materials which can be deeper studied and analyzed. A significative step in this evolution of the experimental equipments has been the development of synchrotron radiation which allows a high brilliance and intensity of light to be applied as radiation source to any of the already known experimental techniques such as X-ray diffraction, infrared spectroscopy, X-ray fluorescence, imaging, among others. This allows to get information of very small samples, to obtain data of very small parts of a sample, to go deeper in the information, including to map the spatial distribution of data of very small thin films, samples, sections or whatever the sample were prepared. Several examples of SR applications to cultural heritage will be shown, basicaly on the fields of ancient ceramics (lustre decorated Islamic pottery) and ancient paintings. In the examples proposed, the problem to be solved will be identified, as well as the limitations found using classical experimental equipments and the results obtained wth SR.

**Q-IV.02** 17:00

**COPPER NANO-CLUSTERS IN ANCIENT OPAQUE GLASS FROM POMPEII AND SICILY: A XAS STUDY**

R. Arletti, G. Vezzalini, Earth Science Department, L.go S. Eufemia 19 41100 Modena, Italy, and S. Quartieri, G. Sabatino, M. Triscari, Earth Science Department, Salita Sperone 31, 98166 Messina S. Agata, Italy and M.C. Dalconi, Earth Science Department, Corso Ercole I° d'Este, 44100, Ferrara, Italy

Since the beginning of the application of experimental research to the ancient materials, the accuracy of the results has been improved following the chalenges of the needs arising from the study of such materials. Thus, deeper information has been obtained in order to better know the techniques used to built-up or produce a particular material, how and why ancient goods were used, who used them, when, etc.

From the very beginning, the scientific equipments also improved their accuracy while the amount of sample need were reduced in size and/or weight. This open a wide range of opportunities to the research of ancient materials which can be deeper studied and analyzed. A significative step in this evolution of the experimental equipments has been the development of synchrotron radiation which allows a high brilliance and intensity of light to be applied as radiation source to any of the already known experimental techniques such as X-ray diffraction, infrared spectroscopy, X-ray fluorescence, imaging, among others. This allows to get information of very small samples, to obtain data of very small parts of a sample, to go deeper in the information, including to map the spatial distribution of data of very small thin films, samples, sections or whatever the sample were prepared. Several examples of SR applications to cultural heritage will be shown, basicaly on the fields of ancient ceramics (lustre decorated Islamic pottery) and ancient paintings. In the examples proposed, the problem to be solved will be identified, as well as the limitations found using classical experimental equipments and the results obtained wth SR.

**Q-IV.03** 17:20

**MODELLING THE SIZE OF RED-COLOURING COPPER NANOCCLUSERS IN ARCHAEOLOGIC GLASS BEADS**

M.O. Figueiredo, J.P. Veiga, CENIMAT, Fac. Sci. Technol., New Univ. Lisbon, 2829-516 Caparica, and J.P. Mirão, Geophysics C., Évora Univ., 7002-554 Évora, Portugal

Ancient red glasses have been studied to ascertain the origin of colour, attributed either to the presence of both copper clusters and cuprous oxide in Celtic enamels and Gallo-Roman tessarae or to copper alone in Satsuma glasses. A study on valence state and local atomic structure of copper implanted in silica glass assigned the presence of Cu<sub>0</sub> and Cu<sup>I</sup> species. Therefore, the red colour of opaque ancient glasses still calls for further study.

X-ray absorption experiments at Cu K-edge were conducted at the ESRF beam line ID22 on the red layer in a "rosette"-type bead found during excavations at Lisbon Old-City and on selected model compounds (metallic copper and the red oxide, Cu<sub>2</sub>O - the mineral cuprite, with linear Cu-O linkage). To model Cu 1s XANES spectra, a multiple scattering formalism was applied using the FEFF code. A hypothetical tetragonal structure was postulated for Cu<sub>2</sub>O to release constrains from linear O-Cu-O bonds. Assuming clusters of 42 atoms in metallic copper and 56 atoms in modified cuprite, the general trend of calculated spectra compare well to experimental data collected from the red glass. A full discussion is presented on the obtained results.

**Q-IV.04** 17:40

#### CHEMICAL ANALYSIS OF ANCIENT PHARMACEUTICAL PRACTICES

M. Cotte, B. Fayard, J. Susini, ESRF, BP 220, 38043 Grenoble Cedex, France; P. Dumas, Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France; Ph. Walter, (C2RMF), UMR 171 CNRS, Palais du Louvre, Porte des Lions, 14 quai F. Mitterrand, 75001 Paris, France

Our work aimed at a better understanding of the chemistry involved in the synthesis of lead plasters, which were pastes made of lead salts and fat, frequently used in the past as pharmaceutical products. Two non destructive synchrotron based techniques, X-ray micro-fluorescence and infrared micro-spectroscopy were used.

First, ancient Egyptian cosmetics were analysed by synchrotron infrared micro-spectroscopy. This technique allows both organic and mineral components to be identified and located. Furthermore, information about the supra-molecular organisation of the molecules can be obtained. Lead soaps were shown to be highly concentrated within the cosmetic. Second, about 100 recipes of lead plasters, mentioned in ancient texts, were assessed and compared. A selection of formulae has been reconstituted and the kinetics was followed by infrared spectroscopy. The primary chemical reaction involved in the preparation is the saponification of fat by the lead salts. The effect of some crucial parameters such as addition of water or temperature was studied. This chemical viewpoint provided a better insight on the technical evolutions developed over centuries. Finally, the question of the potential toxicity of such lead based products was addressed by analysing the interactions between these lead compounds and skin.

In conclusion, this study shows that although lead plasters exist since more than 30 centuries they yet appear as highly advanced preparations.

19:00

#### **AWARD CEREMONY**

The symposium organizers and the candidates to the graduate student award are requested to attend.

#### **CONFERENCE RECEPTION**

**Session V : Stone, glass, ceramics I**  
**Session chair : G. Padeletti**

- Q-V.01** 9:00 -Invited- LUSTERS OF RENAISSANCE POTTERY: EXPERIMENTAL AND CALCULATED OPTICAL PROPERTIES USING INHOMOGENEOUS THEORIES  
**Serge Berthier**(a), Giuseppina Padeletti(b), Paola Fermo(b), Anne Bouquillon(c), Marc Aucouturier(c) Eric Charron(a), (a)Institut des Nanosciences de Paris, 140 rue de Lourmel, 75015 Paris, France, (b)Istituto per lo Studio dei Materiali Nanostrutturati-CNR, Via Salaria Km.29, 5 c.p. 10 Monterotondo Staz., 00016 Monterotondo(Roma), Italy, (c)Centre de Recherche et de Restauration des Musées de France, Palais du Louvre, Porte des Lions, 14 quai François Mitterrand, 75001 Paris, France  
Lustre decoration of medieval and renaissance potteries constitutes one of the most important and sophisticated decoration technic of the mediterranean basin. Lusters consist in a thin layer of silver and copper nanocrystals immersed in a dielectric matrix. Different physical phenomenons are responsible for the very brilliant and complex colored effect produced by the lusters. On the one hand, according to the tickness of the thin layer, interferential effects occure that give rize to a classical iridescent effect. On the other hand, the nanostructure of the metallic counpound leads to an extra absorption, generally observed in the visible or near infrared, due to an external resonance associated with the excitation of a surface plasmon in the metallic particles. The position of this resonance, and so the color of the film, depends on many parameters, mainly : (1) The relative volum fraction p of the metal inclusions. (2) The mean size of the metal particle. (3) The shape of the particles and (4) the dielectric functions of the constituents. These two phenomenons are not independant as the second one greatly affects the dielectric function the film and so its optical tickness.  
In this paper, we will first present the physical and optical properties of six different lusters, five from Deruta and Gubbio (Italy) of XVI century and one from Asia Minor (XIII century). The structure and the composition of the different films have been determined by scanning electron microscope (SEM), ion beam analyses (PIXE and RBS) and low incidence X-ray diffraction. The optical properties have been determined by two different technics : spectroscopic measurements under various incidences and gonioscopic measurements for a given angle of incidence and wavelength. The first one allows the determination of the effective index of refraction of the inhomogeneous layer, and the second one the determination of the Bidirectional Reflectance Distribution Function (BRDF) of the material.  
A first attempt of modelization is then presented in the fram work of the mean film theory. In spite of a very complex structure, these calculations are in fairly good agreeement with the experimental results.
- Q-V.02** 9:40 -Invited- THE LONGETIVITY OF OLD MORTARS  
**Ioanna Papayianni**, Aristotle University of Thessaloniki, Laboratory of Building Materials, Greece  
The study of Old Mortars has revealed a treasure of knowledge concerning the binders and their use in manufacturing mortars as well as the philosophy on which the building technology of the past was based. In the paper the characteristics of mortars taken from some important monuments with remarkable durability are presented and commented so as their resistance to weathering to be highlightened.  
Comparing them within the frame of modern durability issues it could be said that the principles, on which the design of long resistant materials is based, are diachronious.

Q-V.03 10:20

STUDY OF SULPHATION OF CANDOGLIA MARBLE BY MEANS OF MICRO X-RAY DIFFRACTION EXPERIMENTS

R. Pedrazzani, I. Alessandri, E. Bontempi, L.E. Depero, Laboratorio di Chimica per le Tecnologie, Università di Brescia, Via Branze 38, 25123 Brescia, Italy, F. Cappitelli, Dipartimento di Scienze e Tecnologie Alimentari e Microbiologiche, Università di Milano, Via G. Celoria 2, 20133 Milano, Italy, E. Pantos, CCLRC, Daresbury Laboratory, Keckwick Lane, Warrington WA4 4AD, U.K., L. Toniolo, Istituto per la Conservazione e la Valorizzazione dei Beni Culturali, Sezione di Milano "Gino Bozza", Politecnico di Milano, P. zza Leonardo da Vinci 32, 20133 Milano, Italy

A proper restoration intervention strategy focussed on cultural heritage conservation requires a preliminary phase of investigation of degradation process.

The deterioration of stones exposed to pollution is a complex process, in which chemical, physical and biological mechanisms are involved: the synergistic action of rain, sunlight, wind and atmospheric pollutants induce both physical and chemical weathering processes. This research was aimed at assessing not only the kind of damage caused by microorganisms colonization and atmospheric pollution, but also the effect of previous restoration treatments on a magnificent late gothic church, Milan Cathedral. Based on a matter survey, the façade appears to be very damaged by corrosion, biological patina, black crusts, fractures. These findings were integrated by means of laboratory analyses carried out on materials. Structural and chemical analyses (X-ray Diffraction/Microdiffraction, X-Ray Fluorescence (XRF), IR spectroscopy) were performed on Candoglia marble samples taken from the façade. X-Ray Diffraction is a powerful non-destructive tool to analyse all kinds of materials, both crystals and powders. In particular, micro X-Ray Diffraction (mXRD) allows to perform analysis of micro-areas and micro-quantities also on geometrically complex samples (since no flat surfaces are needed) and to obtain phase identification with a good spatial resolution also by means of laboratory instruments. In this work, X-Ray Microdiffraction experiments were collected also at Daresbury Synchrotron Laboratory, where a high spatial resolution allowed to obtain a deterioration mapping. On the basis of these results it was possible to define the sulphatation effect on marble degradation by characterizing several layers at different depth.

10:40

**BREAK**

**Session VI : Stone, glass, ceramics II**

**Session chair : M. Vendrell**

Q-VI.01 11:00

LASER TECHNOLOGY APPLIED FOR THE ANALYSIS OF ROMAN POTTERY TERRA SIGILLATA

G. Nicolás, M. Mateo, A.J. López, A. Ramil V. Piñón and A. Yáñez, Laboratorio de Aplicaciones Industriales del Láser, Universidad de A Coruña, C/ Mendizábal s/n, 15403 Ferrol, Spain

The significant progresses in technology and instrumentation of these last decades have led to an increasing presence of laser systems in the fields of art conservation and archaeology where they are used as advanced tools for analysis of cultural heritage materials, cleaning of artworks or study of deterioration mechanisms. In the present study, laser induced plasma spectroscopy (LIPS) has been applied for the analysis of shreds of Terra Sigillata, name given to a fine tableware of Roman Era. These ancient ceramics are made with aluminosilicates with a high content of iron and are characterised by a sintered coating (red slip) on a less sintered body of different chemical composition and thickness. The laser based technique appears to be particularly effective to provide information on composition and on elements content variation in depth of both slip and body parts. Furthermore, examinations with scanning electron microscopy coupled with energy dispersive detection of X-rays (SEM-EDX) were also performed to evidence the morphological and chemical differences between specimens investigated. The results reported here concern analyses of fragments of different provenance and quality.

Q-VI.02 11:20

COPPER BLUE IN ANCIENT GLASS BEADS: A XANES STUDY

J.P. Veiga and M.O. Figueiredo, CENIMAT, Fac. Sci. Technology, New Univ. Lisbon, 2829-516 Caparica, Portugal

The results of a non-destructive X-ray absorption study at the K-edge of copper are reported and discussed in relation to the colouring of ancient glasses, namely, "Nueva Cadiz" type tubular blue glass beads recovered from excavations conducted in the Old City of Lisbon.

The XANES study was performed at beam line ID22 of the ESRF. Minerals configuring two distinct blue tonalities due to Cu (2+) in similar square coordination were selected as model compounds: azurite,  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ , which is a classical blue pigment used in ancient wall paintings over plaster, and chalcantite,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , with exactly the blue colour of tubular glass beads manufactured since the Egyptian Antiquity. Experimental Cu 1s XANES spectra are compared to the results of theoretical modelling using the FEFF code based on a multiple scattering approach. A remarkable difference was assigned in the environment of copper ions in model minerals. Beyond two S-atoms, only O-anions plus hydroxyls coordinate copper up to 4.2 Å in chalcantite, while in azurite four copper neighbours are present at distances smaller than 3.3 Å. The spatial density of oxygen close neighbours in chalcantite therefore approaches the real situation of copper in glasses and may explain the "copper-blue" tonality. Raman spectroscopy could be a clue for the problematic but, as a destructive essay, its application is ruled out for such archaeological glass beads as museum pieces.

**Q-VI.03** 11:40

**UNDERSTANDING BRONZE AGE FAIENCE IN BRITAIN AND IRELAND**

Alison Sheridan, National Museums of Scotland, Chambers Street, Edinburgh, U.K., Kathy Eremin, Harvard University, Boston, USA and Andrew Shortland, Oxford University, 6 Keble Road, Oxford, U.K.

An NMS-led international research project is investigating Bronze Age faience beads in Britain and Ireland, to resolve a long-standing debate about their origin. Some had traditionally argued that they had been imported by Egyptian or Mycenaean traders c 1400 BC, but compositional analysis in the 1970s challenged this, demonstrating significant differences in tin content between beads from NW Europe and elsewhere. C14-dating of faience-associated cremated bone now demonstrates that faience was in use in NW Europe as early as the 20th century BC.

The project uses binocular microscopy, X-ray fluorescence spectrometry and controlled-pressure scanning electron microscopy to provide compositional and textural information non-destructively; some beads have also been sampled, for wavelength-dispersive electron microprobe analysis, to provide more accurate comparative compositional and technological information. The results allow us to dismiss the 'Orientalist' hypothesis, confirming the high tin content of many beads, and demonstrating the use of a mixed alkali fluxing agent - the latter a feature of C European faience manufacture, whence the knowhow seems to have come. Production was small-scale and localised. We have also demonstrated, for the first time, that some beads had been worn on the corpse during cremation. Experimental data confirm the analytical findings.

**Q-VI.04** 12:00

**FIRST-TIME OBSERVATION OF MASTRO GIORGIO'S MASTERPIECES BY MEANS OF NON-DESTRUCTIVE TECHNIQUES**

G. Padeletti, ISMN-CNR, cp 10, 00016 Monterotondo Staz. Roma, Italy, P. Fermo, Dip. Chim. Inorg. Met. e An., Univ. of Milano, via Venezian 21, 20133 Milano, Italy, A. Bouquillon, S. Pages-Camagna and M. Aucouturier, C2RMF-CNRS, Palais du Louvre, 75001 Paris, France

For the first time some excellent pieces belonging the majolica production by the great master Giorgio Andreoli from Gubbio (Central Italy), have been characterized from a chemical point of view with the aim to identify the composition of both pigments and luster. A series of PIXE, RBS, and Raman analyses have been performed on some dishes coming from Museo del Palazzo dei Consoli (Gubbio) and Louvre Museum (Paris) lustred by Giorgio Andreoli and decorated by famous majolica painters such as Francesco Xanto Avelli. The three techniques are complementary and useful in the investigation of art objects since they are non-destructive. Furthermore the low detections limits allow the identification of all elements and compounds present and RBS allows concentration profiling. It is worth notice that the examined objects are characterized by the presence of both gold and ruby red luster, a peculiarity of Mastro Giorgio technique. The measurements by PIXE have been carried out by AGLAE instrument at the Louvre Museum. The results are put in relation with a collaborative study on the optical properties of Italian lustred ceramics also described in the present symposium

12:20

**LUNCH**

**Session VII : Paint and paintings**  
**Session chair : M.-C. Corbeil**

**Q-VII.01** 13:30 -Invited-

**CHARACTERIZATION OF WATER-MIXABLE ARTISTS' OIL PAINTS**

**Michael R. Schilling**(a), Joy Keeney(a), Roberta Renz(a), Casey Greet(b), Jesús Jiménez(b), Charles N. Millner(b), V.C. Jenkins(b) and Tom Learner(c). (a)The Getty Conservation Institute, 1200 Getty Center Drive, Suite 700, Los Angeles CA 90049, USA, (b)California State Polytechnic University, 3801 West Temple Avenue, Pomona CA 91768, USA, (c)Tate Millbank, London SW1P 4RG, U.K.

In the 1990s, artists' colormen introduced oil paints that could be thinned with water, which eliminated the need for organic solvents to clean brushes and palettes. These so-called 'water-mixable' oil paints (WMO) were formulated by means of chemical modification and through the use of additives to possess many of the working properties of traditional oil paints, such as buttery consistency and transparency. Today, four manufacturers produce a full line of WMO paints: Artisan (Winsor & Newton), Max (Grumbacher), Aqua Duo (Holbein), and Van Gogh H2Oil (Talens). Because WMO paints are relatively new commercial products, little published information is available about how they can be differentiated by analytical techniques from traditional artists' oil paints, although the patent literature discusses composition in some detail. In this preliminary study, Fourier-transform infrared spectrometry, gas chromatography mass spectrometry and direct temperature-resolved mass spectrometry were used to investigate the chemical compositions of the four unpigmented WMO products (as neat liquids and as dried films), and contrast the results from traditional linseed oil media (cold-pressed, stand, and heat-bodied). The analytical results showed only slight differences between the WMOs and the traditional linseed oils. However, by partitioning the liquid WMOs between water and an immiscible organic solvent (such as toluene or chloroform), it was possible to extract a portion of the WMO additives into the solvent layer. In subsequent analyses, the presence of non-ionic, polyoxyethylene surfactants (POE) was clearly ascertained. Research is presently underway to establish if POEs will provide suitable marker compounds in aged WMO paints.

**Q-VII.02** 14:10 -Invited-

**NEW INSIGHTS INTO PIGMENT PROCESSING IN ANCIENT EGYPT**

**Ph. Walter**, Centre de recherche et de restauration des musées de France – CNRS UMR 171, 14 quai François Mitterrand, 75001 Paris, France

The growing use of analytical techniques based on ion beams, synchrotron radiation or portable X-ray tubes has allowed new opportunities to characterise archaeological pigments. For a few years, we have analysed materials from cosmetics containers, wall painting or funerary stela from Egypt.

Using a portable X-ray fluorescence spectrometer, we have successfully determined in the field the chemical composition of cosmetics used during the Predynastic period and the techniques of an artist who has painted his tomb at Saqqara at the time of Amenophis III (ca. 1350 B.C.). Then, more powerful analytical tools developed in the laboratory or at the European Synchrotron Radiation Facility were applied to quantitatively analyse samples from the Louvre museum: the mineralogical composition, the trace elements in specific pigments, and the microstructure of the crystals were measured to shed new lights on the craftsman techniques. These new data allowed us to describe improvements in the selection and the preparation of specific materials, as well as in the know-how to formulate complex mixtures involving organic binders and pigments.

**Q-VII.03** 14:50

**INVESTIGATION ON WHITE PIGMENTS USED AS MAKE-UP DURING THE GRECO-ROMAN PERIOD**

**E. Welcomme**, Ph. Walter, E. Van Elslande, G. Tsoucaris, Centre de Recherche et de Restauration des Musées de France – CNRS UMR 171, 14, quai François Mitterrand, 75001 Paris, France

Different white pigments were used during Antiquity to prepare white make-up for women faces. Combining observations and elemental analysis with structural information, we were able to characterise the mineralogical composition of cosmetics, the trace elements and the microstructure of the crystals. SEM/EDX analyses enabled us to describe the choices of materials and their preparation by crushing or chemical synthesis to obtain white pigments. In the Hellenistic period, we have mainly found lead white, which has required elaborated synthesis processes. Quantitative X-ray diffraction allowed us to establish different ratio of hydrocerussite  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  and cerussite  $\text{PbCO}_3$ . These data can be linked to the chemical conditions of preparation described by Ancient authors. On the other hand, the analyses of Roman cosmetics from Pompei, Cologne and Amiens show the use of more common materials like gypsum, calcite and kaolin. We will discuss the material properties in relation with the make-up uses and we will try to explain these differences between the two periods.

**Q-VII.04** 15:10

**COPPER RESINATE: AN XPS STUDY OF DEGRADATION**

Claudia Altavilla and Enrico Ciliberto, Dipartimento di Scienze Chimiche Università di Catania, viale Andrea Doria 6, 95125 Catania, Italy

In this work, we describe an X-ray Photoelectron Spectroscopy (XPS) study of Copper Resinate, a transparent green glaze that are coloured by copper salts of resin acids. This pigment was used in Europe in fifteenth and sixteenth centuries, and disappeared from artists' palettes after the end of sixteenth century, because the tendency to discolour was already widely known by artists of this time[1]. An essential prerequisite for work of art restoration is the understanding of the effects of various climatic parameters on the deterioration process[2,3]. For this reason, pictorial models of copper resinate in linseed oil, capable of simulating the ancient paintings on mobile supports have been prepared and aged in a climatic chamber, under different conditions such as exposure to UV radiations, humidity and different concentration of chemical pollutants (NO<sub>x</sub> and SO<sub>2</sub>).

All the samples were investigated by XPS and the data obtained were evaluated in order to estimate aging effects as well as mechanisms of degradation[4]. On these paint layers damage induced by X-ray irradiation was also verified.

[1]Roy, Ashok. Artist's Pigments, A Handbook of their History and Characteristics. vol.2, Washington D.C.: Distributed for the National Museum of Art, Washington, by the Oxford University Press, 1993.

[2]C. Altavilla, E. Ciliberto: Decay characterization of glassy pigments:an XPS investigation of smalt paint layers Applied Physics. A. 79, 309 (2004)

[3]C.Altavilla, E.Ciliberto, Michelangelo's David surface investigations: an XPS approach, EXPLORING DAVID DIAGNOSTIC TESTS AND STATE OF CONSERVATION, edited by S. Bracci, F. Falletti, M. Matteini, R. Scopigno, Firenze 2004, ISBN 88-09-03325-6, printed by GIUNTI.

[4]E. Ciliberto, C. Altavilla: La Chim. L'Ind. 7, 84 (2002)

**Q-VII.05** 15:30

**NMR SPECTROSCOPY: A NEW ANALYTICAL TOOL FOR THE STUDY OF PAINTED ARTWORKS**

Apostolos Spyros, NMR Laboratory, Department of Chemistry, University of Crete, Knossos Ave., 71409 Heraklion, Crete, Greece and Demetrios Anglos, Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), P.O. Box 1527, 71110 Heraklion, Crete, Greece

Nuclear Magnetic Resonance spectroscopy is proposed as an efficient analytical tool in the study of painted artworks. The main focus of the present contribution is the study of the binding medium from two original oil paintings, dated from the early 20th and the late 17th century.

High resolution 1D and 2D NMR experiments established the advanced state of hydrolysis and oxidation of the two original oil paintings. Studies of the solvent extractable component from model samples of various drying oils, raw oil paints and aged oil paints allowed the definition of several markers based on the integral ratios of various chemical species present in the H-1 and C-13 NMR spectra. These markers are sensitive to hydrolytic and oxidative processes that reflect the extent of aging in oil paintings. The first results of the application of the proposed analytical NMR methodology to the study of aging of other binding media used in paintings, such as tempera and acrylics, will be presented. Finally, an analytical NMR study of the composition of different natural varnishes will be attempted, in an effort to identify their contribution in NMR spectra of material extracted from original paintings. The non-destructive nature of the proposed analytical NMR methodology represents a great advantage, since the usually minute sample quantities available from original artwork can be subsequently analysed further by other analytical techniques, if necessary. Furthermore, the use of sophisticated cryoprobes and hyphenated LC-NMR techniques is expected to minimize the amount of material needed to perform NMR analysis of paintings, and make NMR a more favourable technique for the analyst, in view of its rapidity and experimental simplicity.

**Q-VII.06** 15:50

**ONOUFRIOS, THE FAMOUS XVth CENTURY ICONOGRAPHER, CREATOR OF THE "BERATI SCHOOL": STUDYING THE TECHNIQUE AND MATERIALS USED IN WALL PAINTINGS OF INSCRIBED CHURCHES**

E. Pavlidou(a), M. Arapi(b), T. Zorba(a), M. Anastasiou(a), N. Civici(c), F. Stamati(d), K.M. Paraskevopoulos (a), (a)Physics Dept. Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece, (b)Institute of Monuments of Culture, Tirana, Albania, (c)Institute of Nuclear Physics, Tirana, Albania, (d)Institute of Popular Culture, Tirana, Albania

The study of the materials and techniques employed for the wall paintings creation, complementing the information from historical and aesthetic data, contributes in the integrated knowledge for the iconographer and his period.

In the 16th century, regarding the iconography in the former Byzantine area, besides the School of Crete, and besides Francos Catelanos and his school, a third artistic personality who created his own school too, Onoufrios, appeared in the central Albania and expanded his activity as a painter till northern Greece, the nearby areas, Ohrid etc. Inscriptions documenting the works of Onoufrios are found in some of the churches that he decorated with wall paintings: "St. Apostles" (1547) Kastoria Greece, "St. Nicolas" Shelcan Albania, "St. Paraskevi" (1554), Valsh Albania, while are attributed to him the church of "St. Theodores" in Berati, Albania (before 1547) and others.

He is one of the best icon painters of the whole Balkan region and the best painter that had ever worked in Albanian territory. Onoufrios managed to combine the local painting tradition with the best tradition of the eastern (Paleologian) and western (Italian) schools, resulting in a realistic and natural drawing.

He is the creator of the "Berati School" that expanded in other parts of the peninsula. His individual character can be distinguished in the work of his students: his son Nikola (who inherited his style in painting), Onoufrios from Cyprus etc.

Based on careful observations, a number of paint samples were extracted from wall paintings of three of the above mentioned churches. Ground and paint layers were examined using micro-FTIR, Optical Microscopy, FPXRF and SEM-EDS, to characterize materials and methods used by the artist to create these works. Our findings in each church are discussed and compared each other in order to understand how and with what material and resources the painter worked, and how he developed his technique.

The presence of calcium carbonate as the main component, in all FTIR measurements, points to a fresco technique. Pigments like red and yellow ochre, carbon black, green earth, calcium carbonate are used in all cases. The use of gypsum in the plaster construction is characteristic. The deterioration of the wall paintings due to environmental effects -different in every church- is also examined.

16:10

**BREAK**

**Q-VII.07** 16:30

**TECHNIQUE AND PALETTE OF XIIIth CENTURY PAINTING IN MONASTERY OF MILESEVA**

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The monastery of Mileseva is one of the most important Serbian spiritual centers. ?iographers recorded that the erection of Mileseva started in 1234. The Church, architecturally belongs to the Raska School, that was characterized by the Romanesque type of building and is composed by one main building with two lower chantries. Narthex was built around 1235 to bury Archbishop Sava.

Nowadays Mileseva is mainly known for its frescoes. The first group of frescoes was produced in the 1230s. In the second half of the XVI cent., the church was repainted and only fragments have survived. Newer frescoes were damaged in a fire, but they happened to save the earlier and more valuable paintings from the XIII cent. The fresco examined in our study belongs to the XIII cent. fresco. This was uncovered nowadays and was cleaned only by distilled water and thus the samples taken were from the first old painting.

The materials and techniques used were determined by means of micro-analytical techniques. The strong presence of the characteristic peaks of calcite, in all FTIR spectra obtained from the substrate as well as from painted layers confirms the use of the fresco technique. Furthermore, in all studied samples a thin yellow organic layer on substrate's surface was detected (imprimatura). FTIR spectra of this layer indicate the use of egg.

The combination of micro- FTIR and SEM-EDS elemental microanalysis revealed the existence of Lapis Lazuli in blue colours and green earth in green colours. The application of Lapis Lazuli in Byzantine hagiography as blue colour is known mainly in portable icons, because of its high cost, which makes its use in large amounts prohibited. Its appearance in particular wall painting confirms that a wealthy person funded the hagiography of this church. In the sample taken from Angel halo three different layers were found. With SEM-EDS was verified that the first is a metallic layer; of thickness 10-12 μm containing pure silver while the third (2-3μm) is gold. As was found by FTIR spectra animal glue was used to stick gold on silver surface.

**Q-VII.08** 16:50

TRANSPARENT SURFACE COATINGS: MICRO-ANALYTICAL STUDIES ON GREEK POST-BYZANTINE ICONS

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Icons are portable panel paintings whose production began as early as the first centuries of the Byzantine Empire (330-1453). The surface of those paintings was protected by thick, mostly transparent coatings, which have darkened over the centuries. Furthermore, new layers were applied on top of them, thus resulting in icons that are presently smothered with multiple surface coatings, often covering their original aspect. The main objective of the present study is to characterise these coatings on Greek post-Byzantine icons.

Samples were taken from a number of representatively selected icons. Their layer build-up was initially observed in cross-sections using light microscopy (LM). Direct temperature resolved mass spectrometry (EI-DTMS) and on-line TMAH methylation Curie-point pyrolysis gas chromatography mass spectrometry (Py-TMAH-GC/MS) analysis led to the detection, in all samples, of oxidised diterpenoid acids. Moreover, triterpenoid-derived compounds and monoesters present in beeswax were identified in many cases. The free and/or network-bonded palmitic and stearic acids, together with the isotopes of lead, seem to derive from linseed oil that has been mixed with a lead-containing dryer. The presence, in some cases, of lead carboxylates was further confirmed using imaging-Fourier transform infrared spectroscopy (imaging-FTIR). In a single case, elementary analysis using scanning electron microscopy-energy dispersive X-Ray spectroscopy (SEM-EDX) validated the application of a copper-based glaze.

The examined icons are covered with aged surface coatings, in particular layers of varnish, glaze, and/or plain oil. The mass spectrometric data supplied structural information on the compounds present in them, whereas light and chemical microscopy was used to study the individual layer composition as a function of the variations within that layer. However, the ageing effects and the interaction between the surface coatings are still issues that are currently being investigated in connection to the exact composition of each individual layer.

**Q-VII.09** 17:10

QUANTITATIVE CHARACTERISATION OF PIGMENT MIXTURES IN PAINTINGS BY FIBRE-OPTICS DIFFUSE REFLECTANCE SPECTROSCOPY

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Fibre-optics diffuse reflectance spectroscopy (FORS) was used to characterise pigment mixtures in paintings. Measurements are non invasive, without any contact to the work of art. They can be performed in situ, at the conservation place.

Our protocol was validated thanks to modern gouache samples: 9 pure gouaches were used as references and 27 binary mixtures of these pure gouaches were studied. Reflectance spectra were processed through Kubelka-Munk theory in order to get scattering and absorption coefficients of the references. We assumed a linear dependence of these optical properties with the Pigment Volume Concentration (PVC) of the gouache layers, so the protocol enabled qualitative as well as quantitative interpretation of the reflectance spectra measured on binary mixtures of references. Indeed, for most cases, numerical processing of FORS-measurements performed on a mixture led to the identification of the components. Besides, once the components were identified, we were able to compute their respective proportions with an accuracy of 5 %.

We had the opportunity to apply those conclusive results on Georges Seurat's last palette. Quantitative characterisation of the 9 pure oil paints and numerous binary mixtures on the wooden panel enables a better understanding of Seurat's pictorial technique as well as chromatic system.

RAPID IDENTIFICATION OF PAINT BINDING MEDIA USING LD-FTICR MASS SPECTROMETRY

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The increased attention in the study of artefact, for the purposes of conservation and restoration, has stimulated many scientists in applying mass spectrometer techniques in order to identify and characterize organic materials used by artists in the past.

Here we report the examination of some naturally occurring organic dyes performed by a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTMS). Coloured organic materials enter into the composition of precious movable cultural heritage principally as dyestuff in textiles and as pigment on illuminated manuscripts or on paints. Before the application of industrially produced synthetic dyes only natural products were available and much effort has been done to find out in the natural world colour sources. Natural dyes come from different things, such as insects and plants.\*Many approaches employed in the identification of dyes generally are chromatographic, i.e. TLC and HPLC, and spectroscopic methods such as FTIR and analysis in UV and VIS regions. The application of FTMS technique allows two principal advantages: the possibility of solid sample direct analysis, without any preliminary time consuming sample treatment, and very small sample quantity use due to very high resolution.

The Institute of Ancient Manuscripts of Yerevan (Armenia) provides us samples of dyes used in the restoration of illuminated manuscripts, reproduced according to the medieval recipes by extraction from natural substances.

The solid dyes were solved or mixed in a suitable solution and spread, like liquid dyes, on a cellulose disk to simulate the analysis of a paint or manuscript samples.

The FTMS mass spectra of all pigments examined exhibit distinct fragmentation patterns among of different pigments thus suggesting that these patterns could be useful in characterising these compounds. The presence of a metallic compounds, necessary for mordant dyes didn't affect the analysis