TECHNART 2009

Non-destructive and Microanalytical Techniques in Art and Cultural Heritage

Athens, 27 - 30 April 2009

PROGRAM and ABSTRACTS

TECHNART 2009 LOGO

TECHNART 2009 logo shows an ancient bronze statue of Venus, the goddess of love and beauty. The statue is dated back to the Roman period and exhibited in the National Museum, Damascus, Syria (No 4309). The photo, courtesy of the Syrian Ministry of Culture, was taken during on site micro-XRF and LIBS measurements (PROMET campaign in Syria).

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BOOK OF ABSTRACTS EDITORS:
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Preface

Dear colleagues, dear friends,

Welcome to Athens and Technart 2009.

Following the organization of Technart 2007 in Lisbon, Portugal, we are very happy to have the opportunity to organize the second conference in this series, Technart 2009, in Athens, Greece, from April 27 to 30, 2009.

We hope that Technart 2009 will provide a lively forum, to present and promote the use of state-of-the-art analytical techniques in the field of Cultural Heritage, offering an outstanding and unique opportunity for exchanging knowledge on the latest advances in analytical instrumentation, methodology and applications. Particle (neutrons, ions) and photon probes, generated at large infrastructures, bench-top or even mobile instruments, but also mass spectrometric and separation techniques, implemented separately or in a combined and synergistic methodology, offer nowadays unique means for advanced and non-destructive characterization, imaging and remote sensing of cultural heritage materials. The contributions at Technart 2009 highlight these new developments and the multidisciplinary character of the rapidly emerging field of analytical techniques in cultural heritage presenting exciting studies of objects and materials in the context of archaeology, art history and conservation science.

To this end, we are very happy to have the opportunity to publish selected papers presented in Technart 2009 in a special issue of Analytical and Bioanalytical Chemistry (Springer).

Finally, we would like to thank all of you, who contributed with their papers in Technart 2009, generating a vibrant scientific program. In addition, we express our sincere appreciation to the members of the International Scientific Committee and the Local Organizing Committee that were involved in the organization of this conference.

Financial support from our sponsors and industrial exhibitors (NCSR "Demokritos", European X-Ray Spectrometry Association, Acutech Ltd., Amptek Inc., Analytical Instruments S.A., Anelis E.E., Bruker AXS, Forth Photonics, Innov-X Systems, Horiba Scientific, Renishaw and Rigaku) is gratefully acknowledged.

We wish to all of you a great conference and a pleasant stay in Athens,

Andreas G. Karydas and Demetrios Anglos

Technart 2009 Co-chairs

Proceedings of TECHNART2009

Special Issue in Analytical and Bioanalytical Chemistry

Selected contributions, based on abstracts evaluation by the TECHNART 2009 International Scientific Committee, will be invited to submit a full or review paper to a special issue of Analytical Bioanalytical Chemistry (ABC). Submitted papers will be assessed following the high standards of peer review of ABC with regard to analytical innovation and significance of results.

ABC is a major international journal in the field of analytical science publishing high-quality research articles on fundamental and applied topics of analytical and bioanalytical science with broad impact.

CONFERENCE PROGRAM

Monday, 27 April 2009

8:30-9:20		Registration
9:20-10:30		**INNOVATIVE TECHNIQUES & METHODOLOGIES I** *Session chairs: A.G.Karydas, D. Anglos*
9:20		Welcome address
9:30	O1 Invited	**The construction of the big monuments in Ancient Egypt: New insight from elemental and structural analysis** G. Demortier
10:00	O2 Invited	**What can confocal x-ray microscopy do for investigations of art and cultural heritage?** B. Kanngießer
10:30		Coffee break
11:00-12:50		**INNOVATIVE TECHNIQUES & METHODOLOGIES II** *Session chair: C. Fotakis*
11:00	O3 Invited	**Raman Microscopy, pigments and interfaces with arts and archaeology** R.J.H. Clark
11:30	O4	**The technological study of renaissance bronzes with the help of neutron imaging techniques** R. Van Langh, E. Lehmann, A. Kaestner, S. Hartmann and F. Scholten
11:50	O5	**X-ray tomographic microscopy compared to ion polished paint cross section of 19th century paints with and without metal soap aggregates** J. J. Boon, E. S .B. Ferreira, J. Van der Horst, M. Stampanoni and F. Marone
12:10	O6	**Analytical techniques for understanding the execution procedures used to craft large bronze masterpieces along the centuries** S. Siano
12:30	O7	**Painting techniques and state of conservation of wall paintings in St. Nicolas church at Zagori-Greece** S. C. Boyatzis, A. Terlixi, G. Pavlopoulos, A. Karabotsos, E. Tziamourani, N. Minos and E. Ioakimoglou
12:50		Lunch break

Monday, 27 April 2009

14:00-15:30		**INNOVATIVE TECHNIQUES & METHODOLOGIES III** *Session chair : R. V. Grieken*
14:00	O8 Invited	**On site analysis of artifacts excavated from Egypt by using newly developed portable diffractometer and fluorescence spectrometer** I. Nakai, Y. Abe, K. Takahashi, N. Kawai and S. Yoshimura
1430	O9	**Fluorescence and vibrational spectroscopy for the analysis of the ageing of selected natural varnishes** A. Nevin, D. Comelli, I. Osticioli, G. Valentini, L. Toniolo and R. Cubeddu
14:50	O10	**NMR spectroscopy in cultural heritage materials analysis** A. Spyros
15:10	O11	**Unlocking documentary antiquities with AXSIA multi-spectral imaging** R.T. Macfarlane, P. Rossi, A.J. Antolak, P. Kotula, B.L. Doyle and S.M. Bay
15:30		Coffe break
15:30-16:50		**CONFOCAL X-RAY MICROANALYSIS AND IMAGING** *Session chair: Z. Smit*
15:30	O12	**Non-destructive, depth resolved investigation of historical glass objects by 3D micro X-ray fluorescence analysis – X-ray tube and synchrotron radiation measurements** I. Mantouvalou, K. Lange, T. Wolff, M. Pagels, L. Lühl , O. Hahn and B. Kanngieβer
16:10	O13	**3D imaging with a confocal μ-PIXE arrangement** N. Grlj, M. Žitnik, P. Pelicon, D. Sokaras, A. G. Karydas and B. Kanngießer
16:30	O14	**3D micro-XRF analysis of Ancient Attic black glazed ceramics** D. Sokaras, E. Aloupi, A.G. Karydas, V. Kantarelou, I. Mantouvalou, B. Hesse, L. Lühl and B. Kanngieβer
16:50-17:30		**VENDORS SESSION (BRUKER-AXS, FORTH PHOTONICS)** *Session chairs: A.G.Karydas, D. Anglos*
17:30-19:00		**POSTER SESSION I** *Session chairs: I. Rabin, Z. Kis*
19:00-21:00		Welcome Reception

Tuesday, 28 April 2009

9:00-10:30		**OPTICS AND LASERS** *Session chair: I. Schechter*
9:00	O15 Invited	**Identification and topography of pigments and varnishes by different optical techniques** M. Elias
9:30	O16	**Filamentation driven terahertz time-domain-spectroscopy for the analysis of cultural heritage related materials** J.-M. Manceau, C. Fotakis and S. Tzortzakis
9:50	O17	**Insights into the use of red lakes in wall paintings by Masolino from in situ analysis and examination of microsamples** D. Comelli, A. Gallone, A. Nevin, I. Osticioli, G. Valentini, L. Toniolo, A. Longoni, R. Albert and R. Cubeddu
10:10	O18	**Compositional depth-profiles of excavated marble patinas and possible use in authenticity investigations** K. Polikreti and C. Christofides
10:30		Coffee break
11:00-12:50		**NEUTRONS** *Session chair: V. Argyropoulos*
11:00	O19 Invited	**Non-destructive neutron analysis techniques at ISIS** W. Kockelmann and E. Godfrey
11:30	O20	**Neutron diffraction measurements for the characterization of four Japanese artworks of Tokugawa age** F. Grazzi, L. Bartoli, F. Civita and M. Zoppi
11:50	O21	**Investigation of the content of ancient Tibetan metallic Buddha statues by means of neutron imaging methods** E. H. Lehmann , S. Hartmann, M. Salque and M. O. Speidel
12:10	O22	**Spatial element distribution from prompt gamma activation imaging** Z. Kis, L. Szentmiklósi, T. Belgya, Zs. Kasztovszky and The Ancient Charm Collaboration
12:30	O23	**Multifunctional encoding system for assesment of movable cultural heritage** V. Tornari, E. Bernikola, K. Hatziyannakis, W. Osten, R.M. Grooves, M. Georges, T. Cedric, G.M. Hustinx, J. Rochet, E. Kouloumpi, M. Doulgeridis, T. Green and S. Hackney
12:50		Lunch break

Tuesday, 28 April 2009

14:00-15:30		**SYNCHROTRON RADIATION** *Session chair: J.J. Boon*
14:00	O24 Invited	**Combined use of x-ray milli- and microprobes for non-destructive analysis of large cultural heritage artefacts** K. Janssens, J. Dik, G. Van Der Snickt, M. Alfeld and K. Rickers
14:30	O25	**Material studies on the Dead Sea scrolls** I. Rabin, O. Hahn, T. Wolff, A. Masic, and G. Weinberg
14:50	O26	**A diffusion study of medieval ferrous products using trace elements microanalyses: the case of Italian armours** S. Leroy, P. Dillmann, B. Gratuze, R.Simon, L.Bertrand, A.Williams and P.Fluzin
15:10	O27	**Investigation of celtic ceramic sherds with a laboratory 3D micro x-ray fluorescence spectrometer** C. Seim, L. Lühl, S. Steiner and B. Kanngieβer
15:30		Coffee Break
15:50-16:30		**DIAGNOSTIC TECHNIQUES IN CONSERVATION** *Session chair: H. Brecoulaki*
15:50	O28	**The monitoring of indoor museum environments and the impact of their conservation of their corrosivity on complex organic materials** M. Odlyha, S. Jakiela, C. Theodorakopoulos, J.M. Slater, R. Campana, S.Kutsarova, C.J. Bergsten, A.Cavicchioli, D.L.A. de Faria, A. Niklasson, J.-E. Svensson, T. Grontoft, E. Dahlin and M. Scharff
16:10	O29	**The use of Near Infrared spectroscopy to characterize the state of historic silks** P. Garside, J. Kim and P. Wyeth
16:30	O30	**Preliminary study on the wood from an ancient roman rostrum** E. Caponetti, F. Caruso, C. Di Stefano, M. L. Saladino, A. Spinella, P. Tisseyre and S. Tusa
16:50	O31	**EDXRF and FTIR combined studies of archaeological artworks in Crete** N. Maravelaki and N. Kallithrakas-Kontos
17:30		Tour to Acropolis

Wednesday, 29 April 2009

9:00-10:30 MOBILE SPECTROSCOPY I

Session chair: S. Siano

9:00 O32 Invited **The IAEA activities related to applications of nuclear analytical techniques for characterization and protection of cultural heritage objects**
A .Markowicz, D. Wegrzynek and E. Chinea-Cano

9:30 O33 **Quantitative X-ray fluorescence analyse of an Egyptian faience pendant and comparison with PIXE**
L. De Viguerie, A. Duran, A. Bouquillon, V. A. Sole, J. Castaing and P. Walter

9:50 O34 **Novel extensions of pulsed Raman and laser induced breakdown spectroscopy (LIBS) in art conservation**
I. Osticioli, N.F.C. Mendes, S. Porcinai, A. Cagnini and E. M. Castellucci

10:10 O35 **A novel portable XRF spectrometer: first application to a gilded bronze from the Florence baptistery**
A. Migliori, P. Bonanni, N. Grassi and P.A. Mando

10:30 Coffee break

11:00-12:50 ORGANIC MATERIALS

Session chair: C. Milliani

11:00 O36 **Macromolecules in art and archaeology**
M.P. Colombini

11:30 O37 **From egg tempera to oil on canvas: Analytical study of the evolution of the Post-Byzantine techniques**
E. Kouloumpi, G. Lawson and V. Pavlidis

11:50 O38 **Coloured glazes on silver leaf: Identification of the protein media used in the grounds and coatings**
C. Tokarski, M. Richter, S. Schafer, N. Garnier and C. Roland

12:10 O39 **Parchment characterization and deterioration assessment using optical methods**
B. Dolgin, Y. Chen, V. Bulatov and I. Schechter

12:30 O40 **Comparison of extraction methods for the analysis of natural dyes in historical textiles by HPLC**
I. Karapanagiotis, L. Valianou and C. Chryssoulakis

12:50 Lunch break

Wednesday, 29 April 2009

14:00-15:30		**MOBILE SPECTROSCOPY II** *Session chair: A. Nevin*
14:00	O41 Invited	**The new version of the portable XRD system of the LANDIS laboratory and its application for the non-destructive characterization of ancient pigments** F.P. Romano, G. Pappalardo, L. Pappalardo, F. Rizzo and G. Gatto Rotondo
14:30	O42	**A portable, vacuum-chamber equipped XRF-instrument, designed for the sophisticated needs of the KHM, Vienna** K. Uhlir, G. Buzanich, M. Griesser, C. Streli, P. Wobrauschek, D. Wegrzynek, A. Markowicz and E. Chinea-Cano
14:50	O43	**A combined use of FORS, XRF and Raman spectroscopy in the study of mural paintings in the Aosta valley (Italy)** L. Appolonia, D. Vaudan, V. Chatel, M. Aceto and P. Mirti
15:10	O44	**Micro-XRF and LIBS analysis of gilded bronze figurines at the national archaeological museum of Damascus** V. Kantarelou, A. G. Karydas, D. Sokaras, A. Giakoumaki, D. Anglos, L. Mahfoud, A. Kurdab, M. Azar, A. Almansour and J. Alshehne
15:30		Coffee Break
15:50-17:10		**COMBINED ND TECHNIQUES** *Session chair: P. Mirti*
15:50	O45	**Reliability of optical microscopy, X-Ray diffraction and X-Ray fluorescence for studying tesserae from mosaics** V. Perdikatsis, Ch. Apostolaki, V. Kantarelou
16:10	O46	**Using Micro-XRF and Raman Spectroscopy for non-invasive analysis of Artworks: techniques and applications** E. Lancelot
16:30	O47	**Multitechnique characterization of lapis lazuli for provenance study by means of Ionoluminescence** A. Lo Giudice, M. Albonico, S. Calusi, E. Colombo, E. Conz, L. Giuntini, M. Massi, P. Olivero, G. Pratesi, A. Re and E. Vittone
16:50	O48	**The use of a diamond cell for the FTIR characterization of binding and pigments in contemporary paintings** Z.E. Papliaka and E.A. Varella
17:10-18:30		**POSTER SESSION II** *Session chairs: M. Castillejo, C. Tokarski*
21:00		Gala Dinner

Thursday, 30 April 2009

9:00-13:30		**SENSING AND SPECTROSCOPY** *Session chair: K. Polikreti*
9:00	O49 Invited	**Non destructive identification of art objects using multispectral images and spectra combined with acoustic microscopy** G. Karagiannis
9:30	O50	**Principal component analysis of reflectance medium infrared spectra for the non-invasive identification of organic materials in wall paintings** A. Daveri, F. Rosi, C. Miliani, G. Verri, P. Benedetti, B. Brunetti and F. Pique
9:50	O51	**Second and third harmonic generation measurements of glues used for lining of painted artworks** G. Filippidis, K. Melessanaki and C. Fotakis
10:10	O52	**Micro-fading spectrometry: investigating the wavelength specificity of fading** A. Lerwill, A. Brookes, J. H. Townsend, H. Liang, J. Thomas and S. Hackney
10:30		Coffee break
11:00-12:40		**ION-BEAM ANALYSIS AND COMPLEMENTARY TECHNIQUES** *Session chair: G. Pappalardo*
11:00	O53	**Analysis of Venetian-type glass from Lezha, Albania** Ž. Šmit, F. Stamati, N. Civici, A.Vevecka, M. Kos and D. Jezeršek
11:20	O54	**Elemental analysis of ancient glass beads by means of combined ion-beam and synchrotron-based analytical tools** D. Sokaras, A. G. Karydas, A. Oikonomou, N. Zacharias, K. Beltsios, V. Kantarelou, L. Lühl, B. Hesse, I. Mantouvalou and B. Kanngießer
11:40	O55	**Croatian Apoxiomenos – metal composition and lead provenance study** D. Mudronja, M. Jakšić, S. Fazinić, I. Božičević, V. Desnica, Ž. Pastuović, D. Krstić, J. Woodhead and Z.A. Stos-Gale
12:00	O56	**The hoard of Beçin - non-destructive analysis of the silver coins** M. Rodrigues, M. Schreiner, M. Melcher, M. Guerra, J. Salomon, M. Radtke, M. Alram and N. Schindel
12.20	O57	**Non-destructive determination of the silver content in Roman coins dated to 308-311 A.D. by combined use of the PIXE-alpha, XRF and DPAA techniques** F. Rizzo, G.P. Cirrone, G. Cuttone, A. Esposito, S. Garraffo, G. Pappalardo, L. Pappalardo, F.P. Romano and S.Russo
12:40		Lunch break

Thursday, 30 April 2009

14:00-15:30 X-RAY MICROANALYSIS AND COMPLEMENTARY TECHNIQUES

Session chair: E. Aloupi

14:00	O58 Invited	**μ-EDXRF and XRD on lead-based glazes** M.L. Carvalho, A. Guilherme and J. Coroado
14:30	O59	**Important considerations on applying X-Ray microanalysis techniques for damage assessment of outdoor copper based monuments** V. Argyropoulos, A. Vossou, K. Polikreti, D. Charalambous, I. Sianoudis, A.G. Karydas, V. Perdikatsis, S. Bittner and M. Mach
14:50	O60	**EDXF imaging of Pb depth penetration in glazed ceramics using a micropattern gas detector** A.L.M. Silva, J.F.C.A. Veloso, C.A.B. Oliveira, A.L. Gouvêa, J.M.F. dos Santos and M.L. Carvalho
15:10	O61	**Indonesian painting: Characterization of modern Balinese painting by Raman microscopy** M. R.. Marcelino, S. Lopes and V.S.F. Muralha
15:30	O62	**Use of X-Ray-based microanalytical methods for explanation of origin and corrosion of copper-based pigments** S. Svarcova, D. Hradil, J. Hradilova, E. Kotylanova and P. Bezdicka

POSTER SESSION I
Monday 17:30-19:00

Optics and Lasers

P1 **THE ITALIAN PAINTING OF THE 17TH CENTURY CONTRIBUTIONS OF A NON-DESTRUCTIVE INVESTIGATION**
C. FRANCESCHI, E. FRANCESCHI and S. VASSALLO

P2 **SEC/MALLS TECHNIQUE IN PAPER DEGRADATION STUDIES**
T. ŁOJEWSKI and K. ZIĘBA

P3 **ASSESSING EARLY PHOTOSYNTHETIC GROWTH ON MONUMENTS BY IN VIVO CHLOROPHYLL FLUORESCENCE**
A.Z. MILLER, A. DIONÍSIO, M.F. MACEDO and C. SAIZ-JIMENEZ

P4 **CHARACTERIZATION OF DAMAGES INDUCED BY LIBS ANALYSIS ON ARCHAEOLOGICAL OBJECTS USING OPTICAL PROFILOMETRY**
G. NICOLAS, T. CTVRTNICKOVA and M.P. MATEO

P5 **A NEW SPECTRAL IMAGING APPROACH FOR THE IN-SITU ASSESSMENT OF THE CLEANING INTERVENTION ON STONEWORK**
A. LOUKAITI, V. PAPADAKIS and P. POULI

P6 **NON-DESTRUCTIVE DEPTH-PROFILING OF PHOTO-AGED DAMMAR VARNISH USING SPECTROSCOPIC ELLIPSOMETRY**
K. POLIKRETI and C. CHRISTOFIDES

Neutrons

P7 **POTSHERDS FROM THE INNER MONGOLIA**
R. GILLES, Y.M. SIOURIS, W. KOCKELMANN, M. HOELZEL, D. VISSER and M. BRUNELLI

P8 **ARCHAEOMETRY RESEARCH OF LITHIC RAW MATERIALS FOR EARLY NEOLITHIC PREHISTORIC COMMUNITIES WITH PGAA**
ZS. KASZTOVSZKY, K. T. BIRÓ, A. MARKÓ, T. TEZAK-GREGL, M. BURIC and R. SOSIC

P9 **RADIOGRAPHY DRIVEN PGAI AND NEUTRON DIFFRACTION MEASUREMENTS ON TEST OBJECTS DESIGNED FOR THE 'ANCIENT CHARM' PROJECT**
Z. KIS, L. SZENTMIKLÓSI, T. BELGYA, ZS. KASZTOVSZKY, W. KOCKELMANN, G. FESTA, A. KIRFEL, P. KUDEJOVA, R. SCHULZE, K. T. BIRÓ, K. DÚZS, ZS. HAJNAL and D. VISSER

P10 **TOF-ND AND LIPS COMBINED STUDIES OF ANCIENT BRONZE FIGURINES**
S. SIANO, J. AGRESTI, L. BARTOLI, A.A. MENCAGLIA, A. RASTRELLI

and M. MICCIO

P11 **NON-DESTRUCTIVE CHARACTERISATION OF SILVER/COPPER COINS USING TOF NEUTRON DIFFRACTION**
I. M. SIOURIS, W. KOCKELMANN and V. POULIOS

P12 **METHODOLOGY FOR LARGE SAMPLE NEUTRON ACTIVATION ANALYSIS OF CULTURAL HERITAGE OBJECTS**
F. TZIKA, T. VASILOPOULOU and I.E. STAMATELATOS

Synchrotron Radiation

P13 **STUDY OF METALLIC COMPONENTS OF HISTORICAL ORGAN PIPES THROUGH SYNCHROTRON RADIATION X-RAY MICROFLUORESCENCE IMAGES AND GRAZING INCIDENCE X-RAY DIFFRACTION**
L.K HERRERA, A. JUSTO, A. MUÑOZ and G. MARTINEZ-CRIADO

P14 **STUDY OF JOSEFA D'OBIDOS AND BALTAZAR GOMES FIGUEIRA PAINTINGS BY FTIR AND IN-SITU AND SYNCHROTRON XRF: ASSIGNING AUTORSHIP?**
A. GUILHERME, S. PESSANHA, M.L. CARVALHO, S. VALADAS, T. FERREIRA, C.T. COSTA, A. CANDEIAS, J. CAETANO, R. SIMON and J. MIRÃO

P15 **COMPOSITION OF ROMAN MURAL PAINTINGS FROM SOUTHERN PORTUGAL: SOURCES, COLOUR AND CONSERVATION**
A. CANDEIAS, A. GUILHERME, S. PESSANHA, M.L. CARVALHO and J. MIRÃO

P16 **EVALUATION OF CONSOLIDATION TREATMENTS ON WATERLOGGED ARCHAEOLOGICAL WOOD BY MEANS OF SYNCHROTRON LIGHT X-RAY MICROTOMOGRAPHY**
S. BUGANI, S. CAGNO, P. CLOETENS, M.P. COLOMBINI, G. GIACHI, K. JANSSENS, J.J. ŁUCEJKO, F. MODUGNO and L. MORSELLI1

Diagnostic Techniques in Conservation

P17 **LASER CLEANING OF AGED SHELLAC FROM WOOD**
M. ALIGIZAKI, A. POURNOU, K. MELESSANAKI

P18 **AN EVALUATION OF REFLECTANCE-ABSORPTION INFRA RED SPECTROSCOPY FOR IN SITU INVESTIGATION OF ORGANIC COATINGS ON CORRODED METALS**
S. C. BOYATZIS, V. ARGYROPOULOS, A. SIATOU, K. POLIKRETI, D. CHARALAMBOUS and A.M. DOUVAS

P19 **CHARACTERISATION OF FOXING STAINS IN XVI-XIX CENTURY DRAWINGS USING μ-EDXRF**

M. MANSO, S. PESSANHA, A. GUILHERME, M. AFONSO, A. C. ROCHA, A. BAPTISTA, F. FIGUEIRA and M.L. CARVALHO

P20 ANALYTICAL CHARACTERIZATION OF POLYMERS USED IN CONSERVATION BY ATR-FTIR SPECTROSCOPY
R. CHERCOLES, M. SAN ANDRÉS, J.M. DE LA ROJA and M. GÓMEZ

P21 ASSESSMENT OF GASEOUS AND PARTICULATE MATTER POLLUTANTS IN A BRAZILIAN MUSEUM
R.H.M. GODOI, B.H.B. CARNEIRO, A.F.L GODOI, V.P. CAMPOS, T.M. TAVARES, H. EVANGELISTA5, Y. MAKAROVSKA, V. KONTOZOVA-DEUTSCH, S. POTGIETER-VERMAAK, S. DESCHERMAYER and R. VAN GRIEKEN

P22 STUDY OF THE MORPHOLOGY OF IRON GALL INKS USED IN THE COPY-PRESS PROCEDURE
A. KAMINARI, A. ALEXOPOULOU and E.M. BUCKLEY-DHOOT

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I. KARATASIOS, M. KLIAFA and M. DOULGERIDIS

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ABSTRACTS

ORAL PRESENTATIONS

THE CONSTRUCTION OF THE BIG MONUMENTS IN ANCIENT EGYPT: NEW INSIGHT FROM ELEMENTAL AND STRUCTURAL ANALYSES

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Introduction

In many books on Ancient Egypt, no difference is made when discussing the building techniques used in the Ancient Kingdoms (4500 years B.P) and the New Kingdoms (3000 years BP). During the period of New Kingdoms and at later times, big monuments were made with moderate size stones maintained close to each others with dovetails carved in the adjacent parts of the external blocks of the walls. Nothing similar is visible on the blocks of the Chéops pyramid. By comparison with the 147 m of that pyramid, the height of the monuments of the New Kingdom does not exceed 20 m. We have then calculated that monuments of the New Kingdom (like the Ramesseum whose surface on the ground is similar to the one of the pyramid of the Cheops pyramid) would have required 20 times less work than for the great pyramid. Monuments with the same surface on the ground would accept the same number of workers and the comparison is certainly pertinent. Considering that the works on monuments at different periods are so different and that the structures of the block assembly are very different, we conclude that the materials could be also different.

Experimental

In 1978, the French chemist Joseph Davidovits rejected the usually reported technique of carved and hoisted blocks. He proposed that the building method involved the moulding on site: blocks are made of a kind of concrete whose basic binding element was natron : a sodium carbonate extracted in a region of the North of Egypt, on the left bank of the Nile, very close to the site of Giza (1). Natron, lime and water form caustic soda, which reacts with aluminous limestone to yield the basic geopolymer. To confirm the first analytical **XRF** and XRD results reported in the basic work of Davidovits, we have performed elemental analyses by PIXE (Particle-Induced X-ray Emission) and PIGE (Particle-Induced gamma-ray Emission) and structural characterization by NMR-Spectroscopy (2).

Results

One of the pyramid’s sample appeared to be made of a central compact structure surrounded by a material of a different aspect. The central part was identified as natural limestone but the outer part contains a large amount of F, Na, Mg, Al, Si. The concentration ratios in the binder relative to the core is 7.5 for F, 8.5 for Na, 12 for Mg, 2 for Al and 21 for Si. Recent measurements at higher proton energies on a large number of samples (about 50) confirm these results and indicate, for several ones, a very high concentration (more than 10%) of S and/or Cl The high concentration of sodium, sulphur and chlorine is attributed to the use of natron and the presence of Mg, Si and Si to the use of the Nile alluvium. Furthermore, a significant signal of As in the outer part may be attributed to some additional ore which could be scorodite. A mineral ore containing arsenic was added to produce sodium arsenate acting as an activating ingredient that could have been used in various concentrations to control the speed of the hydraulic setting. Independent measurements in US and France by Barsoum, Ganguly and Hug have recently confirmed our elemental and structural analyses to conclude that the material is synthetic (3). Many other arguments (including: chaotic organisation of shells in the blocks, with respect to their parallel alignment in natural stones in the quarries around Giza , high water content measured by the transmission of electromagnetic waves, traces of mortar mostly at the base of the blocks) play in favour of a mode of construction by agglomeration of limestone aggregates. The walls of narrow channels (with a section of 20 cm x 20 cm, starting from the Queen's chamber of the Cheops pyramid), investigated with a robot by R.Gantenblink clearly show that they were not carved. (4).

The whole calculation of the manpower has been made and our model is corroborated by ancient reports in Latin, Greek and in hieroglyphs. Recent alternative models of construction are also discussed. New investigations by an interdisciplinary team are in project.

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WHAT CAN CONFOCAL X-RAY MICROSCOPY DO FOR INVESTIGATIONS OF ART AND CULTURAL HERITAGE?

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Introduction

During the past six years the novel method 3D Micro-XRF was developed and established at synchrotron sources as well as in the laboratory [1,2,3]. 3D Micro-XRF relies on a confocal set-up formed by two X-ray optics, one in the excitation channel and one in the detection channel. A sketch of the principal set-up can be seen in Figure 1. With 3D Micro-XRF it is possible to perform depth resolved elemental analysis and layer thickness determination in the micrometer regime. In 2006 the confocal concept was transferred to Micro-PIXE analysis with the same aims: to obtain depth resolution in the micrometer regime and to resolve three-dimensionally the elemental distribution in a sample [4,5].

Just from the beginning one main field of application of the two twin methods was art and cultural heritage. As diverse as the investigated objects are, are the questions behind the investigations.

In the talk the basic experimental features are explained and the possibilities and restrictions of both methods are discussed. On the basis of examples the wide range of application is outlined.

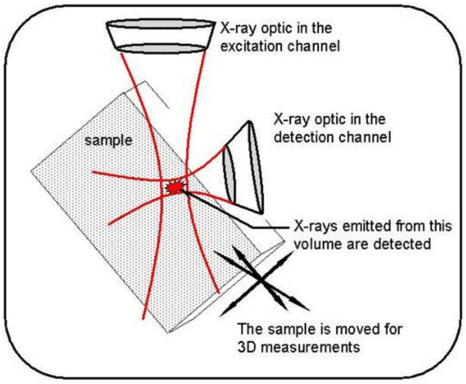

Figure 1. *Sketch of the principal set-up of 3D Micro-XRF.*

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RAMAN MICROSCOPY, PIGMENTS AND INTERFACES ITH ARTS AND ARCHAEOLOGY

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Introduction

Raman microscopy is a light scattering technique used primarily in the characterisation of vibrational modes of molecules and thereby molecular structure. It provides a very effective means of identifying minute grains of any material such as a pigment. The technique has high specificity, sensitivity, reproducibility, spatial (1 μm) and spectral (1 cm^{-1}) resolution, and is both non-destructive and applicable *in situ*. It is thus highly appropriate to the study of materials for which sampling may be either undesirable or forbidden. Such research leads to the identification of pigments on manuscripts, paintings, postage stamps, papyri, icons, ceramics, stuccoes and archaeological artefacts, and leads to the establishment of artists' palettes at different periods and in different localities. At the arts/science interface, information is obtained which bears upon restoration, conservation, and dating of artefacts, and with the detection of forgeries (Best et al. 1995; Clark et al. 1995; Burgio et al. 1997; Clark and Gibbs, 1997; Clark and Curri, 1998; Clark, 2002; Smith and Clark 2004).

Experimental

Research has primarily been carried out using a Renishaw 1000 Ramascope spectrometer with He-Ne and Ar-ion lasers of various wavelengths and low powers. Many complementary techniques, atomic and molecular, were frequently used to confirm or substantiate pigment identifications, notably XRF, XRD, IR and LIBS (Burgio et al., 2000).

Results

Important recent case studies on artwork and artefacts will be reviewed (Clark, 2007). Thus:

Pigment identifications on the immensely valuable codex, the Lindisfarne Gospels, have shown that the blue pigment thereon and thought for centuries to be lazurite is in fact indigo. Hence there is no need to postulate the existence of a trade route from Afghanistan to Northumbria in NE England in 715 AD when the Gospels were constructed; it was indigo which was used, and this material was readily extractable from the indigenous woad plant. Similar studies on eight Gutenberg Bibles have enabled comparative pigment studies to be made.

Extensive art-historical research and Raman spectroscopy on the painting "Young Woman seated at a Virginal" has led to persuasive evidence consistent with its having been painted by Vermeer. Many studies on icons have shown how the pigments present at various depths may indicate the presence of overpaintings.

The first scientific studies of archaeological finds at Samarra, Iraq, made by Sarre and Herzfeld in 1911 have now been carried out on 9th C stuccoes, revealing strongly pigmented illuminated fragments.

The range of pigments used on 16th – 18th C Islamic manuscripts has been shown to differ only slightly from that found for secular ones (Burgio et al. 2008).

Extensive studies of kaolinitic clays and ceramics have shown that the anatase (titanium dioxide) found therein is an extraordinarily intense Raman scatterer, leading to its ready detection even at 0.1 weight% levels (Clark et al. 2007).

Finally, recent studies have shown that Bourdichon, in his famous French miniatures of c. 1500 AD, used metallic bismuth as a mid grey (Burgio et al., in press).

Conclusion

Rarely has an optical technique made such an impact on seemingly unrelated disciplines.

Acknowledgements

The skilful research of my associates, most recently Drs L. Burgio, T. D. Chaplin, A. M. Correia, R. R. Hark, A. Jurado-Lopez, S. Brown, G. D. Smith, and J. Van der Weerd is gratefully acknowledged.

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THE TECHNOLOGICAL STUDY OF RENAISSANCE BRONZES WITH THE HELP OF NEUTRON IMAGING TECHNIQUES

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Introduction

Neutron imaging has proven to be an alternative tool for non-destructive investigation complementary to common X-ray techniques. This is of particular importance for metals, where the penetration of neutrons is higher than X-rays can provide. In cases where lead, bismuth, gold or silver is involved in thicker layers, neutron imaging is the only tool for transmission investigations.

On the other hand, neutrons provide high contrast for hydrogenous materials like resins, adhesives, wax and lacquer. Therefore it is possible to visualize such kind of materials within the environment of thick metallic layers. In the past years, advanced neutron imaging techniques have been developed [1, 2, 3], which are all based on digital detection systems. Beside the transmission radiography (high resolution and dynamic) also three-dimensional structures can be observed with tomography methods.

Experimental

The neutron tomography facility at the NEUTRA imaging beam line (SINQ, PSI, CH) was used to inspect a group of thirteen Renaissance bronze statuettes from the Rijksmuseum Amsterdam. The beam size of up to 40 cm fits well to the dimensions of the objects. The objects were rotated around their vertical axis in steps over at least 180° and the projections were used to reconstruct the entire volume with mathematical tools. When the size of the object exceeds the beam size, advanced reconstruction methods have been applied [4].

Results

The obtained image data can be used to indentify which kind of casting technique has been used. A distinction is made between a direct and an indirect casting technique. Neutron inner material properties like inclusions, cracks, historic restoration treatments, can be made visible. Material thickness and sample dimensions can be measured and compositional differences can be identified. This information is extremely relevant in understanding bronze casting techniques in the Renaissance and later periods, and can be used to determine oeuvres of artists. Some data have been used to produce animated videos to visualize the improved understanding of the Renaissance bronzes.

Conclusions

The described neutron imaging methods can be applied to study technical art historical aspects of three dimensional objects in a non destructive method, when it is impossible to visualize the interior of an object using more traditional tools like X-ray and videoscopy. The facilities at PSI are available on demand for dedicated studies

Figure 1: *Example of a Mercury sculpture as reconstructed from the tomography data. It is e.g. possible to visualize and to measure the size and distribution of empty volumes with the help of specialized software tools*

Acknowledgements

This work was performed at PSI and funded by the Rijksmuseum Amsterdam, The Netherlands.

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X-RAY TOMOGRAPHIC MICROSCOPY COMPARED TO ION POLISHED PAINT CROSS SECTIONS OF 19TH CENTURY PAINTS WITH AND WITHOUT METAL SOAP AGGREGATES

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Introduction

Synchrotron based X-ray tomographic microscopy is an innovative and novel way to examine paint cross sections. Instead of embedding, grinding and polishing, a paint sample is not sectioned at all but studied afterwards in the computer which reconstructs the three dimensional distribution of the pigment particles, media and other features.

Experimental

Experiments on paint chips (maximum size 500 micron wide) were done on the TOMCAT beam line (TOmographic Microscopy and Coherent rAdiology experimenTs) using an X-ray energy of 40 kV. Acquired data sets at 350 nm or 700 nm resolution were analysed with custom made software and the commercial Avizo 3D imaging program with large data set plugin using a 64 bit quad-core CPU with 8 Gb RAM and a dual graphic card with 1 Gb on board. This amount of computing power was found suitable for the paint chip data sets consisting of 2048 tiff images of 1024x1024 pixels. In this way virtual sections were obtained in the XY, XZ and YZ direction. Virtual sections were then compared with paint cross sections of the same samples made in the traditional way albeit ion polished in stead of hand polished. Ion polishing was performed on a JEOL Cross Section Polisher (CP) using a 4-7 keV Argon ion source (1). The resulting 2D sections were investigated in a high resolution Field Emission SEM (FEI XL30). Metal soaps were identified with imaging FTIR microscopy (BIORAD).

Results

The tomographic microscopy technique was applied to a multilayer lead white containing paint from a mid 19th century panel painting by the Dutch painter J. Bosboom (1817-1891) and a sample from a preprimed commercial canvas with severe lead soap formation from the estate of the American Hudson River School painter F.E. Church (1826-1900). This approach allowed the inspection of the paints in three dimensions without the limitation of only one plane observable in traditional paint cross sections. Layer structure and particles can be visualized in 3D and even in stereoview. Metal soap aggregates could be modeled in 3D while the lead white pigment distribution shows large empty spaces where lead white has reacted to lead soaps. Mineralization by reaction with atmospheric carbon dioxide to lead carbonates can be detected and modeled in 3D. The relationship between reactive layers and still intact areas is evident by comparing virtual sections. In the panel painting sample, the layer distribution and pigment distribution could be reconstructed in virtual space. The SEM of the ion polished sections positioned after 3D analysis show how accurate the virtual sections are despite a lower spatial resolution compared to SEM at high magnification.

There are still difficulties to overcome when lead white is present. Very high beam energies have to be used to overcome beam stopping because of the lead even in tiny paint samples. The usefulness of cryo-imaging/experiments is tried presently and will be discussed. Some scattering also occurs thus affecting the resolution. These drawbacks are almost absent when lead free samples are investigated. An example of a calcareous ground with microfossils (Foraminifera) from a painting by the Swiss painter Cuno Amiet (1968-1961) will be shown for comparison. The microfossils could be modeled in 3D and subsequently identified.

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O6

ANALYTICAL TECHNIQUES FOR UNDERSTANDING THE EXECUTION PROCEDURES USED TO CRAFT LARGE BRONZES MASTERPIECE ALONG THE CENTURIES

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Introduction

The contribution of the natural sciences to the knowledge of casting, assembling, and finishing techniques used to craft large size copper alloy masterpieces from ancient to recent times is significantly increasing along the last decades. The archaeometallugical approach, based on integrated analytical campaigns including surface examinations, radiographies, compositional and microstructural, studies on the alloys and core materials is becoming a fundamental complement to the interpretation of the artefacts by human sciences.

The restoration represents a unique opportunity for thorough investigations of casting procedures, alloy compositions, surface chiselling, and patination. Fundamental information on the ancient art foundry were achieved during the restoration works of the Riace Bronzes, Marco Aurelio’s Equestrian Sculpture, and the Praying Boy from Rhodes. Besides these milestones, many other studies were carried out on Greek, Etruscan, and Roman large bronzes but still further insights are needed in order to achieve an exhaustive picture.

The topic is even more undeveloped for Renaissance masterpieces. Up to a few years ago the only relevant case study available was those on the *Porta del Paradiso* by Lorenzo Ghiberti (1426-1452), which was carried out at the beginning of the eighties.

Here, an overview of the main concerns of the present topic will be introduced through the statement of the general problems and the presentation of some recent case studies. The interpretation of the execution procedures and the analysis of the material used to craft the *Minerva* from Arezzo, large bronze of Hellenistic style (IV b.C,-I a.C. uncertain dating), the Amore Attis and the David by Donatello (1435-40), and the *Decollazione del Battista* by Vincenzo Danti (1571) were successfully carried out. Furthermore, substantial advancements were achieved on the metallurgical interpretation of the *Porta del Paradiso*.

The discussion of these case studies provides the opportunity for a chronological excursus and a critical review of the present knowledge on the historical development of the art foundry techniques along the centuries.

Results

The five masterpieces mentioned above were thoroughly investigated using several analytical approaches, from naked eye to advanced analytical techniques, such as for examples X-ray radiography, XRF, and XRD, optical and ESEM-EDX microstratigraphy, laser induced plasma spectroscopy (LIPS), μ-Raman, and other

The results achieved for the Minerva from Arezzo significantly contributed to interpret the masterpiece as an authentic Hellenistic sculpture, likely an archetype, against the previous temporal collocation within the Early Roman Empire (I a.C.). Furthermore, the study revealed unknown features of the ancient large bronzes.

Similarly, original data were found on the Renaissance art foundry concerning the evolution of the lost wax technique, casting procedures and alloy compositions.

The comparison of the result achieved for all these case studies with the well-known tradition of commentaries and treatises (Pliny, Theophilus, Cennini, Ghiberti, Gaurico, Biringuccio, Agricola, Vasari, Cellini) confirms that only rarely the descriptions reported in these historical sources are in agreement with examination evidences and analytical data.

Conclusions

Besides the thematic insights on the art foundry, the present contribution also aims at providing a picture of the concrete analytical needs of such a fascinating thematic area.

Acknowledgements

This work was carried out in collaboration with many scholars that will be rigorously mentioned during the presentation. The financial support was provided by the OPD, Florence, project STArT of the Tuscany Region, and Authentico (FP 6, c.n. 044480).

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PAINTING TECHNIQUE AND STATE OF CONSERVATION OF WALL PAINTINGS IN SAINT NICHOLAS CHURCH AT ZAGORI-GREECE

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Introduction

The scientific investigation of materials and techniques used in Byzantine and Post-Byzantine wall paintings is rapidly gaining interest among researchers, as the synergistic use of various physicochemical techniques allows a more detailed inspection in the chemical composition and the degree of degradation of the various paint layers. The present study aims at identifying the pigments in the various layers, establishing the possible existence of an organic binder and scientifically evaluating the state of preservation of the paint layers in the wall paintings of Saint Nicholas church, (village of Vitsa, North Western Greece). To this end, microscopic (optical and SEM), spectroscopic (FTIR) and chromatographic (HPLC) techniques were employed.

Experimental

Visible Light Microscopy (VLM), Scanning Electronic Microscopy coupled with Energy Dispersive X–ray analysis (SEM-EDX), Infra-red spectroscopy (FTIR) and micro-FTIR were used for the identification of pigments. Fluorescence Light Microscopy-staining (FLM-staining), FTIR and micro-FTIR, and Reversed Phase High Performance Liquid Chromatography (RP-HPLC) were used for the identification and assessment of degradation of binding medium.

ResultsThe examination of cross-section samples by VLM and SEM-EDX, combined with FTIR analysis of powder samples enabled (i) the identification of inorganic pigments of the wall paintings (red ochre, yellow ochre, terre verte, malachite, cinnabar and lime), (b) the characterisation of the inorganic constituents in plaster. In addition, decay products (nitrates, oxalates and gypsum) have been identified by FTIR and microbial flora was detected by SEM. The detection of proteins in cross-section samples was achieved by staining with fluorescent dyes (FITC) followed by microscopic observation, as well as FTIR (analysis of water soluble fraction of sampled powders). Finally, HPLC analysis showed egg yolk as the major component in binder of paint layers (see *Figure* 1) and animal glue in plaster.

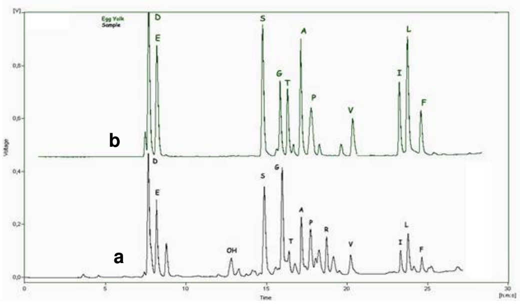

Figure 1: *(a) HPLC chromatogram of hydrolysate from sample (western wall of the monument) and (b) chromatogram of an egg yolk std. sample. Both derivatised with FMOC-Cl. Column 200x4.6mm ODS Hypersil 3μm.*

Conclusions

The information gained from the physicochemical characterisation of materials and the scientific assessment of preservation condition of wall paintings, underlines the necessity for immediate restoration action in Saint Nicholas church, a notable post-Byzantine monument. This also offers an valuable asset to the conservator in the proper decision-making towards efficient treatments.

Acknowledgements

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O8

ON SITE ANALYSIS OF ARTIFACTS EXCAVATED FROM EGYPT BY USING NEWLY DEVELOPED PORTABLE DIFFRACTOMETER AND FLUORESCENCE SPECTROMETER

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Introduction

A new portable X-ray powder diffractometer suitable for field analyses of cultural heritage has been developed. The instrument was brought to several archaeological sites in Egypt, Turkey, Syria and China as well as to the Okayama Orient Museum and MIHO Museum in Japan since 2003 and was subjected to real measurements to test the performances repeatedly. The samples are pigments on pottery, plaster, stone ornaments and stone sculptures dated from second millennium B.C. to modern. The instrument has been improved several times based on these experiences. As the latest revision, we have introduced a function of X-ray fluorescence spectrometer. This modification allows us to carry out high-precision and high-dimensional identification of unknown materials because both crystal structural and chemical compositional information can be obtained from the same sample point of 2mmϕ region. Here, we present the performance of the instrument through the results of on site analysis of excavated objects from an archaeological site at North Saqqara in Egypt.

Experimental

The instrument (Fig. 1) is composed of a goniometer unit, a measurement-controller unit, and a lap-top computer. They can be stored in a portable trunk case with size of 439W×340D×210H mm and a total weight is 15 kg, which is easy to carry by hand. We have adopted Cu X-ray tube and Si-PIN as a detector, which enable us to obtain a good powder diffraction pattern with low background. Moreover, Si-PIN detector has a function of X-ray fluorescence spectrometer. A sample is placed on a θ-rotation axis by using two lazar pointers or ultrasonic sensor, which allows us to carry out nondestructive analysis of a large sample such as statue, wall paintings, etc. The analysis was made at a storage room of the Abusir Poject (dir. S. Yoshimura).

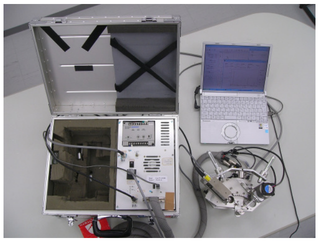


Figure 1. *Portable XRD*

Results

Blue pigments used in ancient Egypt were analyzed by this instrument and were identified as two different pigments, Egyptian blue and Cobalt blue by their chemical compositions and crystal-structural information obtained by this instrument. Figure 2(a) shows the diffraction pattern of the blue pigment of a blue painted pottery found in New Kingdom. The pigment exhibited a diffraction pattern of spinel structure. XRF spectrum of the blue pigment obtained by the same instrument from the same position indicates the existence of Mn,Co,Fe,Ni,Zn (Fig.2(b)) suggesting that the colorant is cobalt blue with a chemical formula of MAl_2O_4 (M=Mn,Fe,Co,Ni,Zn). It is known that the source of the blue pigment is alum from the Western Dessert[1,2]. The blue painted pottery has been found from 18th to 19th Dynasty from this site and transition of the motif is known. Figure 3 shows compositional plots of Mn/Co, Ni/Co, Zn/Co showing a change of the chemical compositions happed between Mid-18th and Late-18th Dynasty.

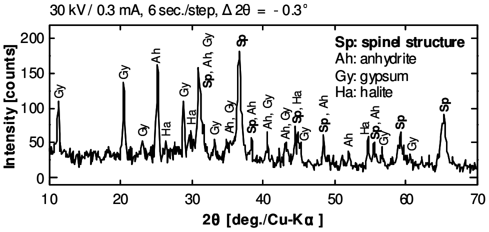
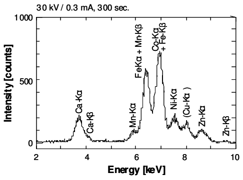


Figure 2 (a). *Powder diffraction pattern of blue pigment*



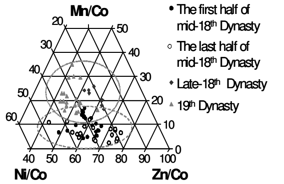


Figure 2(b). *XRF spectrum plot*

Figure 3. *Compositional of the pigments*

Acknowledgements

The P-XRD was manufuctured at X-tec Co. under the direction of Drs. K. Taniguchi and S. Maeo.

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FLUORESCENCE AND VIBRATIONAL SPECTROSCOPY FOR THE ANALYSIS OF THE AGEING OF SELECTED NATURAL VARNISHES

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Introduction

The fluorescence of varnishes and binding media used in paintings is a well known but little understood phenomenon. While yellowing of varnishes is associated with natural oxidation and the development of significant fluorescence emissions with UV excitation, the ageing of varnishes using fluorescence spectroscopy has received only little attention [1,2]. In this work, various naturally and artificially aged natural varnishes have been analysed using fluorescence excitation emission spectroscopy and Fourier transform infrared spectroscopy (FTIR) for a characterisation of potential changes which may occur as a result of artificial ageing of selected materials.

Experimental

Samples were prepared by painting out varnish layers onto quartz substrates using commercially available varnishes from a variety of sources. Diterpenoid and triterpenoids have been considered as have samples prepared using shellac. Models were naturally aged in ambient lighting conditions for 1 year. In parallel a set of samples was artificially aged with broad band visible irradiation at room temperature with a total exposure of approximately 50×10^6 lx.h. This amount of exposure is estimated to be equivalent to 100 years in museum lighting conditions [3]

Spectrofluorimetry was carried out on samples using a John-Yvon Fluorolog bench top instrument for the acquisition of fluorescence excitation emission spectra, with excitation between 275-450 nm and emission monitored from 300-700 nm. In addition, micro FTIR- Attenuated Total Reflectance (ATR) (diamond) spectra were recorded on the surface of samples using a Thermo Nicolet Continuum microscope. Data have been compared for the detection and assignment of changes associated with artificial ageing. Fluorescence excitation emission spectra have also been analysed with multivariate statistical methods for the comparison of data [4]

Results

Significant variation in the fluorescence of materials can be related to differences in chemical composition, which may change with ageing conditions [4]. Molecular modifications of artificially aged varnishes have been detected non-destructively using FTIR and fluorescence spectroscopy. For the comparison of excitation emission spectra, a method based on the projection of excitation and emission data in polar coordinates has been adopted, as is followed by a multivariate consideration of a large set of data. This allows the discrimination between varnishes from different sources and also highlights changes in the fluorescence spectrum which may be related to oxidation following exposure to light. Finally, data from fluorescence can be compared with vibrational spectra recorded with FTIR.

Conclusions

Fluorescence and FTIR spectroscopy may provide useful information for the classification of varnishes, and careful assessment of changes in spectra can be related to chemical modifications within the varnish film. Data can be rationalised with reference to complementary techniques which may provide more precise information regarding the formation of specific oxidation products. The limitations and advantages of the methods proposed will be discussed alongside recommendations for future research.

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O10

NMR SPECTROSCOPY IN CULTURAL HERITAGE MATERIALS ANALYSIS

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Nuclear magnetic resonance (NMR) spectroscopy is an established, state of the art analytical tool in many areas of chemical research, especially when molecular characterization of organic compounds is imperative. Even when one deals with complex mixtures, high resolution NMR spectroscopy can be used to fully characterize specific components, by applying gradient 2D NMR techniques that spread information in two spectral dimensions. Nonetheless, the use of NMR is rather underrepresented in the field of cultural heritage analysis, [1] despite the significant advantages it has to offer, namely the full characterization of molecular structure for organic compounds, the quantitative analysis of multicomponent mixtures of organics, [2] the minimal (if any) treatment of the sample prior to analysis, and the quantitative retrieval of the sample following analysis. In this work, our objectives are as follows:

(a) To present an overview of the earlier literature on applications of NMR spectroscopy in cultural heritage analysis.

(b) To describe the current state of the art with respect to NMR hardware, software and general methodologies that are currently available for the analysis of organic materials.

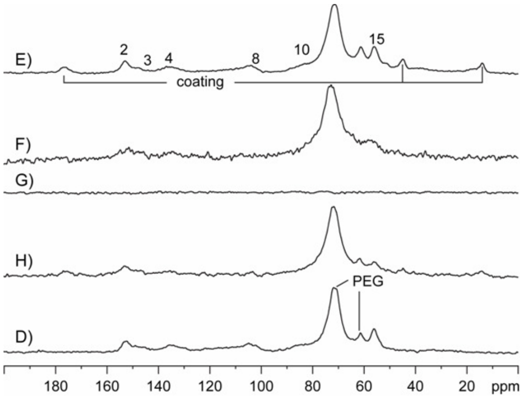

Figure 1: *50 MHz ^{13}C CP-MAS solid state NMR spectra of PEG 4000 conserved archaeological wood samples of the halyard slade excavated from "La Lomellina" shipwreck, from ref. [3]*

The hyphenation of NMR with chromatographic tecniques (LC-NMR-MS), and high resolution 2D NMR in solid samples will be discussed, along with the sensitivity enhancement offered by recent developments in probe technology (micro-, cryo- and flow probes).

(c) To demonstrate the analytical power of modern NMR spectroscopy in the study of organic materials from archaeological and historical context by presenting examples from work that has been conducted during the last few years, some in our own laboratory.

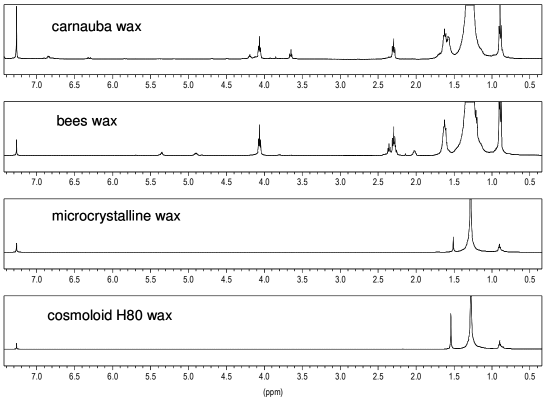

Figure 2: *500 MHz ^{1}H NMR spectra of various natural and synthetic waxes dissolved in $CDCl_3$.*

(d) To suggest possible areas of cultural heritage research that could benefit from the increased analytical capabilities offered by modern NMR spectroscopy methodologies.

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UNLOCKING DOCUMENTARY ANTIQUITIES WITH AXSIA MULTI-SPECTRAL IMAGING

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Introduction

A major cultural enterprise is proceeding to unlock nondestructively a substantial amount of information in ancient documents that remain unread in libraries around the world. Multi-Spectral Imaging (MSI) is a document-deciphering technique applied by BYU that digitizes individual documents in different spectral wavelengths to provide a limited view of hidden text. A shortcoming of the method has been the cumbersome processing of MSI datasets coming from several images of the same area in a manuscript— "image-cubes" —into a more readily deciphered composite image of the text. In this paper, we introduce a potentially powerful new tool for deciphering ancient manuscripts by merging Sandia's AXSIA (Auto-mated eXpert Spectral Image Analysis) with BYU's MSI technique. The AXSIA approach is purely mathematical with no presumptive interpretation of the processed spectral data; BYU's ATIGroup (Ancient Textual Imaging) is primarily interested in accelerated textual access, i.e. tools for interpretation. By accumulating information from the redundant spectral data, AXSIA enables small and unexpected features to be identified automatically without user intervention, and, further, provides a new "synthetic" image that is comprised of multiple correlated images that each carry different pieces of information. The effectiveness of this unique deciphering tool will be evaluated on a particular ancient papyrus owned by BYU.

Experimental and Results

Recently, the ATIGroup has turned its attention to a problematic document, the Tura Codex (P.BYU-Didymos) which presents a compelling palimpsest text. A palimpsest is a manuscript (usually parchment, rarely papyrus) that has been written on, scraped off and reused. In the late-5th/early-6th century AD, sheets of previously used papyrus were erased, assembled into a codex, and overwritten with a commentary on the biblical *Psalms* by Didymos the Blind. The erasure was so effective that the earlier text is essentially invisible to the naked eye. In a few locations in the codex the earlier text peeks around the later text in the pages' margins, but no systematic reading of the older text has succeeded. All attention paid to the Didymos Papyrus since its discovery outside Cairo in 1940 has been directed toward reading the unique, overlying text. The P.BYU-Didymos MSI acquired at various wavelengths have been processed in AXSIA; the resulting image of the underlying text may facilitate greatly a philological deciphering. AXSIA-enhanced textual images have been favorably compared with direct MSI analysis by employing mathematical quality evaluators and also subjective antiquity expert appraisals. Results will be presented here.

Conclusions

The AXSIA-MSI analysis may unlock the underlying text of other manuscripts, and successful application may also bridge to other palimpsest papyri in other European and US collections.

Acknowledgements

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O12

NON-DESTRUCTIVE, DEPTH RESOLVED INVESTIGATION OF HISTORICAL GLASS OBJECTS BY 3D MICRO X-RAY FLUORESCENCE ANALYSIS – X-RAY TUBE AND SYNCHROTRON RADIATION MEASUREMENTS

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Introduction

3D micro X-ray fluorescence spectroscopy (3D Micro-XRF) enables three-dimensional resolved, non-destructive investigation of elemental distribution in samples in the micrometer regime. The quantitative reconstruction of the composition of stratified material by means of synchrotron 3D Micro-XRF has been developed [1] and validated [2], recently. Additionally, a new compact x-ray tube 3D Micro-XRF spectrometer is now available for routine qualitative analysis.

"Reverse painting on glass" comprises a special technique of preparation: glass plates were directly painted with oil- or resin-containing colours from the backside of the object with the resulting optical effect that the glass makes the colours shine intensely. In the presented historical glass piece 'Lüneburger Meditationstafel' of the 14th century black enamel was used as a contour colour. The art historical question concerned the production technique, in particular whether the glass plates were fired after the application of the black enamel colour.

Experimental

Routine measurements were possible with the help of a new compact 3D Micro-XRF spectrometer at the TU Berlin, where the object and special reference samples were investigated. In order to validate the results obtained at the laboratory, 3D Micro-XRF measurements were carried out at the mySpot beamline at the Berlin synchrotron Bessy, which has a dedicated endstation for micro-analysis.

Results

Already the qualitative results obtained with the laboratory setup at the TU Berlin suggest that the altar piece was not fired after painting, though adequate reference black enamel was not available. SR-3D Micro-XRF confirms this assumption thus making suitable restoration procedures possible.

Conclusions

With the help of the new compact 3D Micro-XRF spectrometer non-destructive investigation of historical glass objects is now possible in the laboratory yielding useful qualitative results. For special quantitative questions, 3D Micro-XRF at the synchrotron is up until now necessary.

Figure 1: *'Lüneburger Meditationstafel' of the 14th century:. For the reverse glass painting black enamel was used as a contour colour. Non-destructive depth-resolved measurements show, that the glass plates have not been fired after paint application.*

Acknowledgements

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O13

3D IMAGING WITH CONFOCAL μ-PIXE ARRANGEMENT

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Introduction

One of the methods to study elemental composition of the sample is to analyse its characteristic X-ray spectrum induced by a few MeV ion beam impact (Proton Induced X-ray Emission, PIXE) [1]. Of several approaches to increase chemical, spatial or lateral resolution, one of the most effective is the use of a micro focused proton beam [2]. While it is still very hard to resume a three dimensional elemental distribution in general case, one giant step in this direction represents the introduction of 3D μ-XRF method [3]. The confocal μ-PIXE approach described below allows making a further step towards this goal. The method uses superb lateral scanning capabilities of a proton microbeam, and its potential to analyse thin films, multilayered samples and particles in special 3D samples has been demonstrated recently [4,5]. In this work, we present the tools for reconstruction of sample composition in 3D from a sequence of measured spectra.

Experimental

The confocal arrangement is achieved by alignment of the proton microbeam focal plane with radial beam extension of around 1 μm to the focal point of the polycapillary half-lens that is mounted on the snout of the Si(Li) detector.

The analysed sample was a few tens of micrometers large dust iron ore particle sitting on a nuclepore foil. In order to determine local atomic concentrations in the sample, a sequence of 2D X-ray spectral maps were recorded at several different sample positions along the microbeam axis by scanning the microbeam over a surface area of 100 × 100 μm^2 (Figure 1).

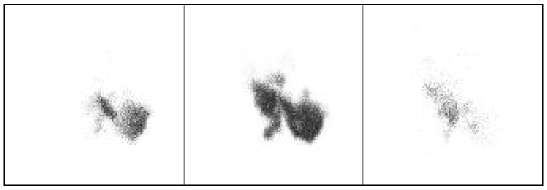

***Figure 1:** Fe K_α X-ray images of an iron ore particle measured with polycapillary lens on Si(Li) spectrometer at three different distances (+50 μm, 0 μm, -50 μm) along the microbeam axis.*

Results

To obtain a 3D image of the particle, it is necessary to write down the X-ray yield of a given element as a function of lateral displacement of the microbeam and of the lateral displacement of the sample from the focal point. The integral equations are replaced by smmations over a finite number of basic volume cells of the sample.

The spatial reconstruction [5] of elemental distribution in aerosol sample has been done without taking into consideration the self-absorption of induced X-rays or the energy loss of protons. The cell area used in summation was 4 μm^2 and due to the small particle sizes a so-called single emitter approximation was appropriate [5]. For matrix element Si such approximation is obviously not good; we had to assume that Si concentration along microbeam path is constant and the yield sequence was fitted by a Gale function. In this work we describe another possible case for the confocal analysis: there is no matrix into which the particle is immersed, but on the other hand the absorption of the emitted X-rays in the sample along the X-ray path towards the spectrometer can’t be neglected, as well as the energy loss of the projectiles.

Conclusions

Confocal PIXE analysis allows in principle the determination of 3D concentration distributions down to a micron spatial resolution. This property can be employed to upgrade the studies of samples having a thick light Z matrix with relevance in cultural heritage (pictorial layers, gemstone inclusions, glazed ceramics etc), or in biomedicine (like frozen biological samples).

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O14

3D MICRO-XRF ANALYSIS OF ANCIENT ATTIC BLACK GLAZED CERAMICS

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Introduction

Ancient advanced glassy nano-materials, like the Attic black gloss that characterises the well known black and red figured Athenian classical vases attracts particular interest concerning manufacturing technology [1]. The attic black gloss originates from specially produced clay colloids which, with firing under a three stage firing procedure, produce a blue black glaze (thickness ~ 25-40 μm). It consists of an amorphous phase rich in polycrystalline magnetite particles with sizes < 200 nm. In general, the attic black gloss can be described as an opaque alkali – alumino-silicate glass which is coloured by fine magnetite crystals. In this work a 3D non-invasive elemental analysis of few selected ancient Greek glazed ceramics is presented. The ceramics belong to well documented collections, recently excavated from the historical centre of Athens and the periphery of Attica dated from 7th to 3rd century BC. The study aims to provide better insight into the elaboration of raw materials used for the production of the clay colloids by means of trace element analysis of the top glassy layer. Such a study cannot be addressed with conventional X-ray based techniques (PIXE, XRF) due to the interference contribution from the ceramic body’s trace elements, so that the implementation of 3D Micro-XRF analysis offers a unique analytical potential.

Experimental

3D Micro-XRF measurements were carried out at the 7T-WLS mySpot beamline of the BESSY II storage ring, Berlin, Germany. The spatial performance of the confocal setup was characterized as ~26μm at the Cu-Kα fluorescence energy and its analytical range covered elements from potassium (Z=19). The samples were scanned through the probing microvolume with a step width of 5 μm, while a 19 keV X-ray incident beam was used. The spatial response and elemental sensitivities were determined experimentally by using modern standard reference glass materials with formalism and procedures described elsewhere [2, 3]. The quantification analysis was based on a minimization algorithm which divides the examined sample into a given (user-defined) number of layers and local densities for the fixed dark matrix as well as fluorescence elements. The local elemental densities and the corresponding thickness for each layer are determined as fitting parameters, whereas key experimental parameters like the elemental sensitivities and FWHM values are allowed to vary within one sigma. In addition, secondary fluorescence enhancement was also included in the quantification scheme resulting in a correction of at least 10% of potassium and calcium intensity profiles [4]. Complementary compositional information regarding the matrix of the black gloss and the calcareous ceramic body (elements with Z=11-14) was supported by PIXE, XRF measurements and literature data [1].

Results

The data analysis provided in a non-invasive way the black gloss layer thickness (~ 30 μm) and depth resolved elemental distributions (local elemental densities) for various major (K, Ca-2nd layer, Fe), minor (Ca-1st layer, Ti) and trace elements (Ni, Zn, Ga, Sr) (Fig.1).

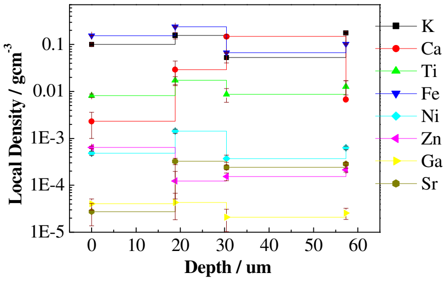

Figure 1. *Local elemental densities in black gloss* (~30 μm) *and calcareous ceramic body, respectively, for an ancient attic ceramic by means of synchrotron 3D Micro-XRF.*

Conclusions

3D Micro-XRF analysis provides advanced analytical information into the depth of a sample. Systematic measurements can answer complex archaeometric questions like the provenance of raw materials.

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IDENTIFICATION AND TOPOGRAPHY OF PIGMENTS AND VARNISHES BY DIFFERENT OPTICAL TECHNIQUES

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Introduction

The recognition of the components of works of art needs non-destructive, contactless and portable methods leading to results in real time. If the identification of a single pigment and dye is already successful by use of diffuse reflectance spectroscopy, the case of pigment mixtures is a new challenge. If these identifications are now workable for superficial layers, the analysis of under layers is in progress in our laboratory using OCT or theoretical radiative transfer.

The analysis of varnishes by use of UV-fluorescence emission spectra, previously implemented in the laboratory on cotton swabs is now directly workable on a real painting. Finally, the imaging of stratified layers by OCT can be applied today to works of art

Experimental

Diffuse reflectance spectra are collected by use of two portable spectrometers, according to the need. The first has a back-scattered configuration [1] with a Xenon lamp and an interferometric UV filter [2] in order to record UV fluorescence emission spectra. The second is a multi-spectral camera which records more than 100 000 000 spectra on the whole work of art.

An original time-domain and full-field OCT device working in the visible range has been specifically developed for works of art and allows 2D and 3D imaging with a 1 µm resolution in the three dimensions [3].

Results

Examples of identifications on real paintings will be presented. In particular, the study of the Joconda will be shown, leading to the identification of two stratified layers, of the artistic technique used by Leonardo and to a virtual removing of the masterpiece [4].

The identification of the resin, the recipe and the ageing of a varnish by UV fluorescence is complicated by the influence of the reflectance of the under pictorial layer and sometimes by the fluorescence of its medium. A protocol will be presented to take into account these difficulties and will be applied to an old painting.

Finally, imaging of varnished violins and of stratified pictorial layers will be shown and the foreseen studies will be approached.

Conclusions

The presented analysis now allows the simultaneously identification of pigments and varnishes with the same instrument, in the exhibition place of the work of art. The results in real time are an important help for restorers who can choose the location of the analysis and repeat it at will.

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O16

FILAMENTATION DRIVEN TERAHERTZ TIME-DOMAIN-SPECTROSCOPY FOR THE ANALYSIS OF CULTURAL HERITAGE RELATED MATERIALS

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Introduction

In this work we explore the application of THz time domain spectroscopy (THz-TDS) in the field of art and in particular for the analysis of painting materials [1]. This is a growing field of research, where only limited work using traditional FTIR spectroscopy has been done and TDS to image hidden drawings [2]. Paintings often contain pigments and colorants, mixed with a binding medium, which are applied in mixtures and in different strata over some kind of support, which may be stone, wood, or plaster; in addition, many paintings are covered with layers of varnish. Thus, a crucial step is the characterization of some natural polymers found in painted artifacts; these include different glues and dairy products, resins and gums, plant oils and waxes.

Experimental

The laser source used is a Ti:Sa femtosecond system producing pulses at 800nm of 35fs duration and 2mJ energy per pulse, operating at 1kHz repetition rate. The laser beam is split in two, in a pump-probe scheme. The pump beam (~800μJ) is focused in air at atmospheric pressure. Before the focal region a BBO crystal (β-barium borate) is inserted, which up-converts part of the fundamental to its second harmonic (400nm). Intense and broadband THz radiation is produced in the 2-color plasma string.

For the transmission measurements we have used a large aperture THz beam, ~50mm in diameter. This approach reduces the errors that could be induced by scattering problems that appear when a focused beam encounters large pigment particles. Samples were prepared according to traditional recipes, and applied on 3mm Teflon substrates. Samples had typical thicknesses found in paintings, in the order of a few hundreds of micrometers.

Results

Transmission spectra have been recorded independently for each binding medium. It is worth noting that varnish has a nearly flat spectral response, but has non-negligible absorption. This could in some cases be a limiting factor, where multiple layers of varnish in significant thicknesses may cover a painting. In this case, powerful filamentation THz-TDS can prove valuable means of revealing spectral details beneath the strong absorption of the covering varnish layers. Following analysis of pure binding media, transmission spectra of pigments mixed with various binders were also recorded.

Comparative measurements between our THz-TDS and an FTIR spectrometer system (BRUKER IFS 66 v/s) were performed. For low absorbing media the two techniques yield similar results. Yet, when it comes to media with higher absorption and/or thicknesses the low signal-to-noise ratio FTIR system quickly reaches its limits while our powerful THz-TDS can still resolve the absorption spectra.

Conclusions

In conclusion, this work demonstrates the advantages of THz spectroscopy for the analysis of highly absorbing artifact materials and confirms the ability for observations beyond thick varnish layers. The extend of absorption measurements to the reflection mode, provides crucial information on the different strata of a painting and other artifacts..

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INSIGHTS INTO THE USE OF RED LAKES IN WALL PAINTINGS BY MASOLINO FROM IN SITU ANALYSIS AND EXAMINATION OF MICROSAMPLES

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Introduction

Renaissance wall paintings by Masolino da Panicale, located at the Baptistery of Castiglione Olona (Italy) and depicting scenes from the life of St. John the Baptist, were analysed on the basis of a multidisciplinary study, comprising both in situ analysis and analytical measurements on selected micro-samples.

The multidisciplinary investigation aims to study the pictorial technique of Masolino, with particular interest on his use of lakes and golden decorations.

Experimental

In situ analysis was carried out using two UV-induced fluorescence imaging devices [1][2], with complementary lifetime and spectral capabilities, in order to identify the presence of organic and inorganic fluorescent materials, such as binders, colorants and lakes, as well as restoration and protective compounds.

Points of interest on the painted surfaces, selected on the basis of the fluorescence imaging inspection, were analysed with a portable X-ray fluorescence apparatus [3], providing complementary elemental information, which can be used to identify inorganic pigments.

Finally, selected micro-samples, partially taken during the present investigation and available from a past restoration activity, were analysed in the laboratory with optical and electronic (SEM-EDX) microscopy techniques

Results

As an example of this investigation, the analysis of the techniques used by Masolino for depicting red-coloured details is provided.

The in situ fluorescence analysis highlighted the presence of an intense red emission detectable in correspondence of different areas on the painting (as, for example, on the red dress of the character of Salomè). The analysis of the related emission spectrum, with two broad peaks at 480 nm and 630 nm, and lifetime mean value (near 3 ns) provided indication on the possible use of madder lake by Masolino.

The analysis of a micro-sample taken from an area on Salomè's dress, with both optical microscopy and SEM (Figure 1), allowed the identification of various layers, including lake pigments, lead white and tin foil possibly covered with gold.

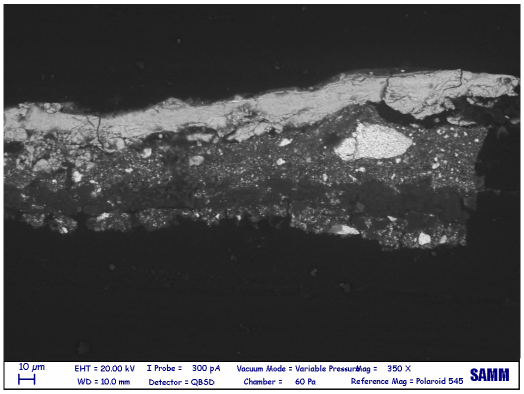

Figure 1: *SEM image of a polished cross-section of a micro-sample taken froma an area on Salomè's red dress.*

Conclusions

Results on the in situ application of UV-fluorescence spectroscopy imaging on wall paintings by Masolino combined with laboratory analysis on micro-samples will be shown. The advantages of using a multianalytical approach, including non-invasive and selected invasive analysis, will be discussed with recommendation for future research and instrumental development.

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COMPOSITIONAL DEPTH-PROFILES OF EXCAVATED MARBLE PATINAS AND POSSIBLE USE IN AUTHENTICITY INVESTIGATIONS

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Introduction

For the last twenty years, a lot of research work has been done on the physicochemical processes involved in the weathering of white, well-crystallised marbles, especially in the field of monument restoration and conservation of archaeological objects. However, data on buried marble patinas is rare and no systematic research has been done to reveal the mechanisms of marble weathering under burial conditions. The detailed study of buried marble patinas would also be great interest to the researchers of ancient marble authenticity investigations given the fact that there is no reliable physico-chemical authentication or dating technique for marble objects [1].

The present work aims to study compositional depth-profiles in buried marble surfaces using laser induced photoluminescence (PL) and LA-ICP-MS and investigate the possibility of using the results in authenticity testing of ancient marble objects.

Experimental

The analysed samples include excavated archaeological samples, samples from building material buried after 1970 and artificially weathered samples. The analyses were carried out on smooth cross-sections of the patinas. Details on the micro-photoluminescence system are given elsewhere [2]. The obtained PL spectrum gives information on the humic and fulvic complexes of Ca existing in the marble patina [2]. LA-ICP-MS gives the profile of several ions ^{25}Mg, ^{27}Al, ^{55}Mn, ^{57}Fe, ^{88}Sr, ^{138}Ba, and ^{208}Pb the concentration changes of which represent the patina weathering front [3].

Results and conclusions

1. According to LA-ICP-MS results, all the detected ions show a concentration decrease from the surface to the marble bulk (Fig. 1) as reported by others [3]. Sr is the only exception probably due to the slow precipitation rate of calcite formation.

2. The concentration of Al stabilizes systematically at slightly lower depths than Mg, Fe and Mn as reported by others [4]. Mg, Fe and Mn are typical impurities of the calcite lattice and their concentration changes may continue throughout the patina, deep into the calcite lattice.

3. The element concentrations reach their bulk values at slightly larger distances from the surface than those at which the humic complexes disappear (Fig. 2) probably because the humates are concentrated in a superficial patina layer.

4. The depth at which Sr reaches its bulk value represents the thickness of the recrystallized calcite layer. These depth values show positive correlation with the burial date of the object. The observation is very important in case of marble objects of ambiguous authenticity.

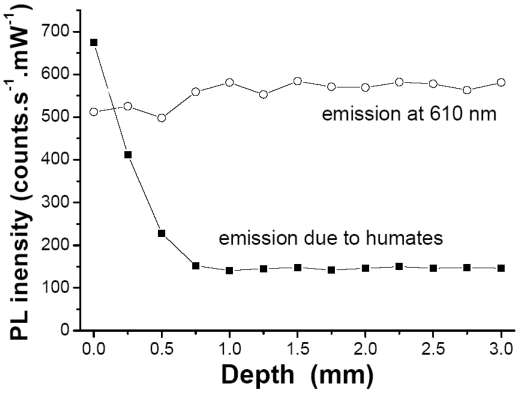

Figure 1. *Typical PL depth-profile of excavated marble surfaces*

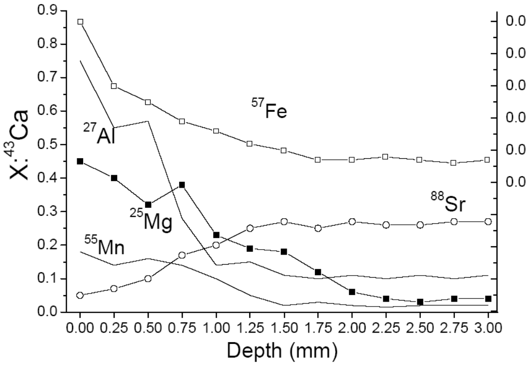

Figure 2. *Typical LA-ICP-MS depth-profiles of excavated marble surfaces. Right axis refers to ^{57}Fe data only.*

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NON-DESTRUCTIVE NEUTRON ANALYSIS TECHNIQUES AT ISIS

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Introduction

Neutron scattering is a vital research and analysis technique for exploring the structure and dynamics of materials and molecules. It provides unique and complementary information to that available from synchrotron light sources. In the past few years, increasing numbers of cultural heritage materials characterisation projects have been carried out at pulsed neutron spallation source ISIS, UK [1]. Neutron-based analytical methods can be used for the non-invasive characterisation of any metal objects including copper [2], bronze [3], and iron [4]. The main advantage is that element, phase and microstructural information can be obtained on the intact object without cutting out a sample of the material.

Analytical methods

Time-of-flight neutron diffraction (TOF-ND) is used for quantitative analysis of metal, mineral, and intermetallic compounds present in a sample. In metals, residual strains, microstrains, and grain orientations can be analysed giving evidence for manufacturing techniques like casting, hammering, and annealing. The structure data are evaluated to obtain estimates of chemical concentrations. For instance, in steel, the cementite content can be analysed by TOF-ND and then used to calculate the bulk chemical composition in terms of weight percent of carbon. Lead added to copper or bronze does not go into solution in the copper and can be directly and accurately determined.

A spectroscopic neutron analysis facility based on neutron resonance capture analysis (NRCA) [5] is currently being developed and installed at ISIS under the EU ANCIENT CHARM project. NRCA uses epithermal neutrons for non-destructive bulk chemical analysis and has particularly good sensitivities for certain heavy elements (e.g. Au, Ag, As, Sb, Sn, Hg).

Energy-selective neutron radiography is currently under development at ISIS which will be used for novel phase contrast methods.

Conclusions

Due to the much lower source intensities compared to synchrotron radiation, neutron analysis techniques are flux-limited, which means that analysed sample volumes are in the order of cubic millimetres. However, the possibility of collecting structural and elemental data non-destructively from many points on one and the same object presents the prospect for many archaeometallurgical applications. This is especially true when the data are combined with typological studies and conventional metallographic data.

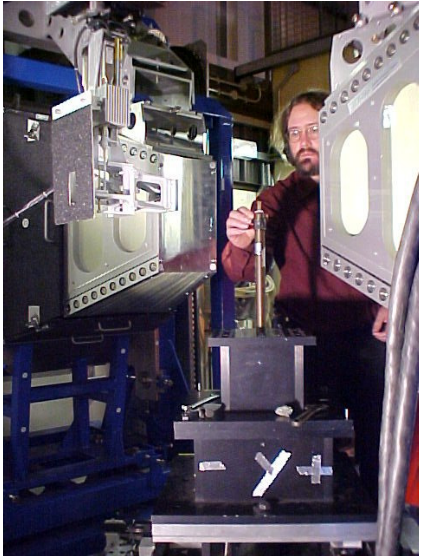

Figure 1: Sample mounting on the neutron strain scanner ENGIN-X at ISIS.

Acknowledgements

Financial support by the EU-FP6 Ancient Charm project No 15311 is gratefully acknowledged

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O20

NEUTRON DIFFRACTION MEASUREMENTS FOR THE CHARACTERIZATION OF FOUR JAPANESE ARTWORKS OF TOKUGAWA AGE

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Introduction

During the Tokugawa age (1600-1868 A.D.) the art of swordsman-ship reached the highest peak in the Japanese history. In this period, weapon-smiting received a strong impulse, furnishing one of the best steel of the history and forging the stereotype of the Japanese swords: the Katana. Wonderful artefacts, also linked to the art of war, were forged. In particular, the protective plate of the sword handle (Tsuba) became an artistic object, made by a peculiar alloy that was carved, patinated, and gilded. The composition of the body, and that of the decorative alloy, is usually unknown, because these were unique pieces, usually patinated, and impossible to be analysed without sampling. Neutron diffraction offers a non-destructive method to investigate the bulk composition of such objects [1,2].

Experimental

We have analysed four Tsubas, from a private collection, three of which were made of steel and one of a copper alloy. All of them are patinated and carved, with some parts showing some gilded and silver filigree. The analysis has been performed using SEM-EDX and neutron diffraction (ND). The latter was carried out on the time-of-flight (TOF) neutron diffractometer INES [3], at the pulsed neutron source ISIS (UK). These experiments included texture analysis, on three of the four Tsubas, using a single axis goniometer.

Results

Rietveld refinement of the ND-TOF results allowed us to quantitatively determine the phase composition of the four Tsubas, to evaluate the carbon content and the presence of martensite (due to the quenching) in the three steel samples and the copper alloy composition in the fourth one [4]. Considering the excellent resolution characteristics of the INES diffractometer [3], the diffraction pattern and peak shape analysis also allowed us to obtain a semi-quantitative information on manufacturing techniques [4,5]. The presence of texture, evidenced by the standard measurements, has been refined and quantified through texture analysis by using the MAUD code [6].

Conclusions

The application of ND to historical artefacts is of great importance for a non-destructive quantitative characterization. Especially for iron artefacts, this method is of paramount importance in determining the carbon content, and the presence of quenching, in order to fully characterize ancient iron and steel artefacts in a totally non-destructive way. A typical diffraction figure of a steel Tsuba is shown in Fig. 1, evidencing the presence of the three phases: ferrite, cementite and martensite.

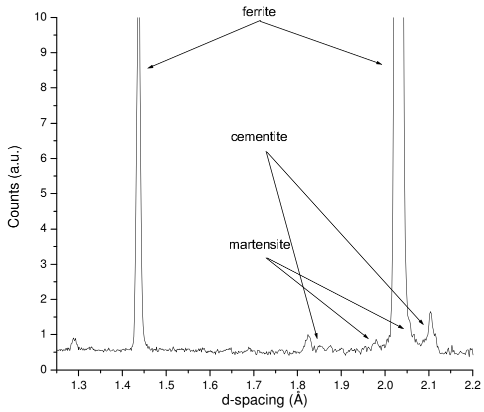

Figure 1: *Diffraction pattern of a steel tsuba showing the presence of ferrite, cementite and martensite diffraction peaks.*

Acknowledgements

The authors acknowledge fruitful discussions with W. A. Kockelmann and E. Godfrey (ISIS, UK).

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INVESTIGATION OF THE CONTENT OF ANCIENT TIBETAN METALLIC BUDDHA STATUES BY MEANS OF NEUTRON IMAGING METHODS

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Introduction

Many important cultural and religious objects from Asia consist of outer metallic shapes, usually bronze, which fully enclose inner contents made of organic materials such as wood, bark, paper, textile, plants and others. Bronze and other metallic materials, such as copper and silver are generally more transparent to neutrons than to X-rays. On the other hand, organic materials are less transparent to neutrons than to X-rays and thus, organic materials, enclosed by metallic materials, can be made visible with neutrons.

Therefore, neutron imaging (radiography and tomography) was found to be an ideal tool for the inspection of objects which consist of metal outside and organic materials inside. This has been successfully demonstrated here with four metallic Tibetan Buddha statues, thus providing archaeometry with a powerful new tool.

The first successful applications of this novel technique are described in the present article. Further possible and useful applications of neutron imaging of cultural objects are outlined.

Experimental

The investigations were performed at the NEUTRA imaging beam line at the spallation neutron source SINQ (PSI, Switzerland) [1]. In standard mode, thermal neutrons are used for both radiography and tomography. A 320 kV X-ray tube can be used alternatively for comparative studies (option XTRA). For high resolution radiography the imaging plate technique [2] was preferred, whereas the tomography study was done with a CCD camera based detector [3]. Four Buddha statues and two stupas were investigated successfully during this pilot project.

Results

As shown in the example of a Buddha Sayamuni in Fig.1 there is no chance to transmit the object with X-rays and to visualize the filling (mostly of organic origin). If the X-ray energy is high, the contrast for organic is low. Contrary, if the photon energy is low, there is no transmission through the metallic over.

This is much better, when neutrons are used. They combine high metal transmission and high contrast for filling materials. Wood, plants, paper, cord was identified inside the objects non-invasively in this way.

***Figure 1:** Comparison of the X-ray image of a Tibetan bronze Buddha sculpture (left) with the neutron transmission radiography image (right): the inner filling content becomes clearly visible because of its organic origin*

Conclusions

The examination of a large number of similar objects is quite easy and straightforward. Although tomography investigations are more demanding, the deliver the full 3D distribution of all materials inside the objects. The PSI installations are available for similar studies on request.

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SPATIAL ELEMENT DISTRIBUTION FROM PROMPT GAMMA ACTIVATION IMAGING

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Introduction

The European collaboration ANCIENT CHARM (http://ancient-charm.neutron-eu.net/ach/) aims to develop new non-destructive neutron techniques to image the internal composition of complex archaeological objects in order to answer various archaeological questions. Among these techniques, Prompt Gamma Activation Imaging (PGAI) and Neutron Radiography/Tomography (NR/NT) form a unique combination, which can determine the 2D/3D distribution of most elements in objects with a non-destructive procedure.

Prompt Gamma Activation Analysis (PGAA) is a well known tool for non-destructive bulk elemental analysis of objects. The measured concentrations are, however, only representative of the whole sample if it is homogenous; otherwise it provides only a sort of average composition of the irradiated part. In this latter case one has to scan the sample to obtain the spatial distribution of the elements.

Experimental

To be able to do sample scanning we have constructed a Prompt Gamma Activation Imaging – Neutron Radiograph/Tomograph (PGAI-NR/NT) setup at the NIPS station of the Budapest Research Reactor, consisting of a high-resolution neutron tomograph and a germanium gamma-spectrometer. The samples are positioned relative to the intersection of the collimated neutron beam and the projection of the gamma-collimator (isocenter) by using an xyzω-moving table.

Systematic sample scans applying PGAI were employed to obtain element maps of an object, which was an imitation of a genuine museum object, a so called replica.

Results

A spatial resolution better than 3 mm has already been achieved in moderately absorbing and scattering matrix of replica. The element maps of the replica for iron and copper are presented. One can see that Fe is concentrated at the perimeter and Cu is distributed more uniformly in the backing.

Conclusions

Often the complete scanning of the object can be avoided and the time of the experiments can be substantially shortened if PGAI is combined with Neutron Tomography or Neutron Radiography. NR/NT produces high-resolution 2D/3D images that characterize the geometrical structure and neutron attenuation features of the object. The elemental composition is to be measured only at selected spots of the object. This makes the technique, called *tomography/radiography-driven PGAI*, much more feasible and cost-effective and provides an automatic image registration between the structural images and elemental distribution.

Acknowledgements

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O23

MULTIFUNCTIONAL ENCODING SYSTEM FOR ASSESSMENT OF MOVABLE CULTURAL HERITAGE

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Introduction

The development of a prototype system and methodology to perform a multiple functioning interferometrically encoded procedure allowing systematic and routine structural impact assessment through time on movable artworks has been elaborated during the EC project MULTIENCODE. It is here described how the artwork is forced to generate self-encoded signals which are used to witness its authenticity and impact versus time.

Experimental

Implementation of non destructive and non contact holographic techniques is being exploited for providing responses of the artwork in the encoded form of fringe patterns. The parametrical usage of the fringe formation allows correlation of one signal to multiple artwork descriptor elements. Descriptor elements form signatures of artwork and can be monitored over time to provide impact assessment and identification of authenticity. The self-encoded fringe representation secures a major anti-fraud and treatment safety advantage in the development of an experimental methodology for a Impact Assessment. The *Impact Assessment Procedure* (*IAP*) has required also development of dedicated hardware and software resulting in hybrid optical geometry and automation algorithms.

Results

Monitoring of sample reactions to aging and impact over time allowed the generation of standard protocol to assess impact. The developed prototype is presented.

Conclusions

It became possible to compare temporally separated interferometric data in order to assess simulated transportation impact and aging (Fig. 1-3), therefore transient interfeormetic signal can characterise an object for restoration, authenticity and anti-fraud measures.

Acknowledgements

This work was funded by EC project MULTIENCODE (FP6-SSPI-00006427)

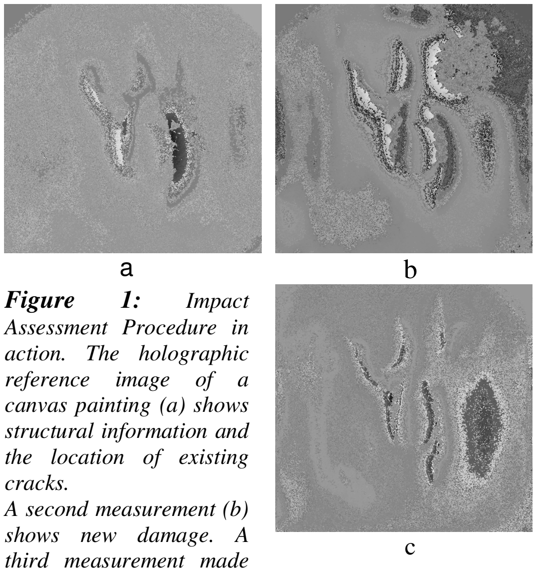

Figure 1: *Impact Assessment Procedure in action. The holographic reference image of a canvas painting (a) shows structural information and the location of existing cracks.*
A second measurement (b) shows new damage. A third measurement made one week later (c) shows the new damage after relaxation of tensions in the canvas.

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O24

COMBINED USE OF X-RAY MILLI- AND MICROPROBES FOR NON-DESTRUCTIVE ANALYSIS OF LARGE CULTURAL HERITAGE ARTEFACTS

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Introduction

Easel paintings can be considered as extended and complex multilayered systems, where a variety of materials of different density and physico-chemical properties is applied on top of each other in various layers.

We have recently demonstrated that by elemental imaging of large areas of canvas paintings and panels, it is possible to obtain, in a completely non-destructive manner, information about buried layers of the pictorial composition that were previously not visible to the naked eye. In this paper, the various parameters that may be altered in order to efficiently perform large-area scanning of painted artefacts will be discussed. Also issues related to safety of the works of art will be addressed. Additionally, the usefulness of combining this manner of X-ray based imaging with high energy X-ray absorption spectroscopy in order to identify the nature of the pigments employed in the buried layers will be illustrated.

Experimental

Vincent Van Goghs 'Patch of Grass' and equivalent mock-up paintings were transported to the microfluorescence beamline L at DORIS-III, a second-generation synchrotron light source at HASYLAB (Hamburger Synchrotronstrahlungslabor at Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany). In the X-ray radiographs of this canvas, the outline of a persons head is (just) visible. A pencil beam (0.5x0.5 mm^2) of quasi-monochromatic synchrotron radiation of 38.5 keV energy was used as primary excitation. With this beam, we scanned a square of approximately 15x15 cm^2, corresponding to the position of the covered head. Dwell time was 2 s per pixel, so that the total scan time was approximately 50 h. Fluorescence spectra were recorded for each pixel with a high-resolution energy-dispersive Ge-detector. The resulting spectra were processed using the software package AXIL to subtract backgrounds and determine net peak areas for all identified elements. The extracted peak areas were adjusted to account for differences in the current of the synchrotron storage ring, detector dead times and spectrum collection times. Elemental distribution images were reconstructed from the resulting sets of peak areas. These maps could be compared with features of the surface painting as well as the X-ray radiographic image.

Results

Most elements found, correspond to the pigments in the top layer of 'Patch of Grass', including various transition metals such as Mn, Co, Fe and Cu. The maps of two elements are directly related to the covered head: Hg and Sb, while some features in the Zn-map are also related to it. Mercury must be associated with vermillion, i.e., the red pigment mercury sulfide. As expected, this pigment was found predominantly in the lips and cheek. The Sb distribution shows a very clear overlap with the lighted parts of the head, but its chemical origin was not immediately obvious. In order to identify the chemical Sb-compound, X-ray absorption near-edge spectroscopy (XANES) measurements were performed on the painting at the X-ray absorption spectroscopy beamline C at HASYLAB at selected positions on the head. The resulting data indicate that Sb_2O_3, a white pigment introduced in the 1920's can be excluded as possible source. The XANES spectra are rather similar to that of lead antimonate yellow (figure 2), a pigment commonly used by Van Gogh. This is be compatible with a slightly yellowish tone of the head, that is typical for Van Gogh.

Conclusions

We conclude that the distribution of Hg corresponds to the red component of the pinkish flesh tones, while Sb relates to a yellowish white. A tri-tonal reconstruction in which the maps for Hg and Sb have been colorized accordingly could be made. This approximate reconstruction presents a significantly clearer and more detailed image of the hidden composition. All physionomical details as eyes, nose, mouth and chin could be visualized. In addition, the reddish intensity of the flesh tones of lips, cheek, and forehead adds to the liveliness of the head.

Acknowledgements

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MATERIAL STUDIES ON THE DEAD SEA SCROLLS

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Introduction

The texts, of great religious and historical significance, known as Dead Sea Scrolls (DSS) were discovered between 1947 and 1956 in eleven caves in and around the Wadi Qumran in the Jordan West Bank. From the very first days their provenance has been playing the central role in the scholar research. In this study we demonstrate the possibility to differentiate between Qumran and non-Qumran production area of the scrolls, coupling non-destructive quantitative analysis of trace elements to spectroscopic investigation of the inks.

Experimental

The analysed samples include inscribed and non inscribed fragments of the Dead Sea Scrolls as well as "dummy" samples of goat parchment inscribed in our laboratory with the inks prepared according to the ancient recipes. The characterization of the samples was made with the following techniques: µ-XRF, 3D-XRF, SEM-EDX, µ-FTIR and µ-Raman.

Results

The water of the Dead Sea and of the springs of the West Shore has a unique ratio of the elements chlorine and bromine [1-3]. This ratio manifests itself clearly in the trace analysis of the inks of the scrolls and to a lesser extent in the parchment. Fig. 1a shows the sharp change on the profile of the ratio in the inscription with the ink containing the water from the Dead Sea vicinity. Fig. 1b displays a similar change in an antique scroll's inscription.

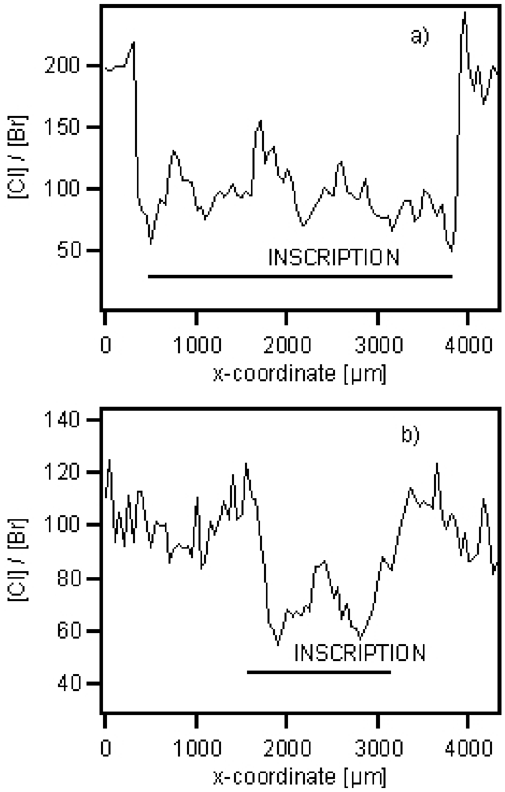

Figure 1: *[Cl]/[Br] profile of the parchment and inks in a) "dummy" prepared with the water from the Dead Sea area; b) Thanksgiving scroll*

Conclusions

The examination of a large number of ancient and artificially prepared samples shows that the ratio of the elements chlorine and bromine in parchment and inks might serve as a fingerprint of the water used in the production process.

Acknowledgements

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A DIFFUSION STUDY OF MEDIAEVAL FERROUS PRODUCTS USING TRACE ELEMENTS MICROANALYSES: THE CASE OF ITALIAN ARMOURS

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Introduction

The study of trade routes and diffusion of ferrous materials is a fundamental topic for history and archaeology. The clarification of geographical provenance of ferrous archaeological products seeks to increase a better knowledge of the history of techniques and economy. A case study of this research is to understand the circulation of high quality medieval steel products during the Middle Ages. Two well-known regions were devoted to this type of production that seems to be linked to the use of manganese rich ores: the French Pyrenees and the Central Italian Alps. In the medieval period, a part of the ferrous and steel industry was dedicated to the production of arms and armours especially in Northern Italy. Several studies have recently highlighted the fact that the Slag Inclusions (SI), embedded in the metallic matrix during solid state reduction processes, lead to crucial information on the origin of the metal. The provenance can be followed by first determining specific trace elemental signatures of the supplying regions, then by following these signatures into the SI remaining in the ferrous products [1]. The present work aims to record the chemical trace element signature of Italian Alps in the SI of a subset of prestigious armours.

Experimental

A variety of techniques was commonly used by our team to obtain quantitative chemical information on trace elements in SI. The main type of SI present in ancient artefacts is fayalitic-rich (Fe_2SiO_4). ICP-MS coupled with Laser Ablation (LA-ICP-MS) is a very efficient method to obtain an accurate quantification of the SI trace elements. Nevertheless, LA-ICP-MS is a destructive method that cannot be used on high museographical value samples as the ones collected on ancient armours. Moreover this method only allows to analyse areas larger than tens of micrometers. Due to the extremely well-preserved condition of the famous Italian armours, only tiny specimens (~3x2mm) were taken on each armour. The SI found in these highly manufactured artefacts are all very small in size (<20x20 μm^2) and can not be destructed even very locally. Synchrotron µ-XRF with a confocal geometry [2] is an especially useful technique to analyse these SI. It allows extremely valuable museum pieces, from which only a tiny sample can be taken, to undergo non-destructive testing.

Results

The trace element signature of several production regions could be defined by analysing ore, slag and semi products representative of the different operating chains. In this way, a subset of prestigious armours samples provided by the Wallace Collection Museum (London) was investigated at the FLUO (ANKA) and the L (HASYLAB) microfocus beamlines in confocal mode so as to record the trace element signature in the SI and verify their compatibility with the hypothetical Italian Alps production centres. During experiments about fifteen inclusions per sample and for 6 armours samples were analysed. Results highlight the fact that one sample doesn't seem to come from Italian Alps.

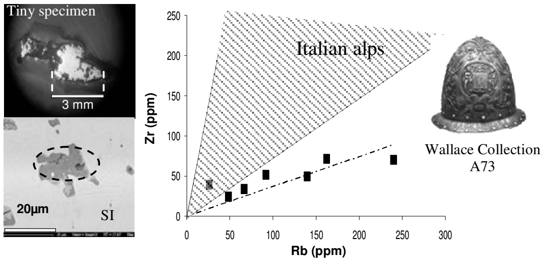

Figure 1: *Comparisons of trace elements variation (Zr versus Rb contents) diagram for the Italian Alps region and sample WCA73*

It is an Italian helmet, made in Milan c1575-90 according historians, and called by English contemporaries a *"Spanish morion"*.

Conclusions

This result reconsiders the historical hypothesis. These quantitative confocal µ-XRF analyses opening up possibilities to obtain information on the origin of some armour samples- something that had not been possible until now.

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INVESTIGATION OF CELTIC CERAMIC SHERDS WITH A LABORATORY 3D MICRO X-RAY FLUORESCENCE SPECTROMETER

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Introduction

3D micro X-ray fluorescence analysis allows depth resolved and non-destructive elemental analysis [1,2].

In cooperation with the Institute for Prehistoric and Scientific Archeology of the University Basel different types of Celtic ceramic sherds (some with a white colour application) were examined with an x-ray tube 3D Micro-XRF spectrometer to evaluate their elemental distribution. Although a quantitative elemental analysis is, until now, only possible when using monochromatic excitation (synchrotron), qualitative analysis can yield valuable archeometric information.

The Celtic ceramic sherds originate from "Basel-Gasfabrik", a big Celtic settlement from about 100 years B.C. [3]. The sherds are cultural assets of Switzerland. Besides the elemental distribution of the ceramic itself, the white coloured decoration on some of the sherds is of special interest, especially if being determined as an engobe. The application of these engobes to ceramic requires a highly developed oven for the possibility to exactly control the burning temperature. If white colour can be identified to be an engobe, evidence of advanced Celtic pottery culture would be proved.

Experimental

Investigative measurements on the Celtic ceramic sherds were made using the 3D Micro-XRF spectrometer at the laboratory at the TU Berlin. Excitation radiation from a microfocus x-ray tube (ifg iMOXS MFR) is focussed with polycapillary full lens, fluorescence radiation transported with a polycapillary halflens onto a Si(Li) detector. The overlap of the foci of the optics forms a probing volume of about 50 µm at 10 keV. In order to characterize the spectrometer, reference foils were examined alongside with the sherds.

Results

The Matrix of the sherds could be compared concerning colour and texture. Differences in clay matrix and white colouring are clearly discernible into the depth of the sample. Some of the white coloured decoration was found to be an engobe, some a thin layer of calcium carbonate.

Conclusions

The measurements show the usefulness of a 3D Micro-XRF spectrometer in the laboratory, even if a quantification procedure is not available until now. The qualitative output of the measurements can already help answer important archeological questions. In this case a distinction between different manufacturing processes was possible.

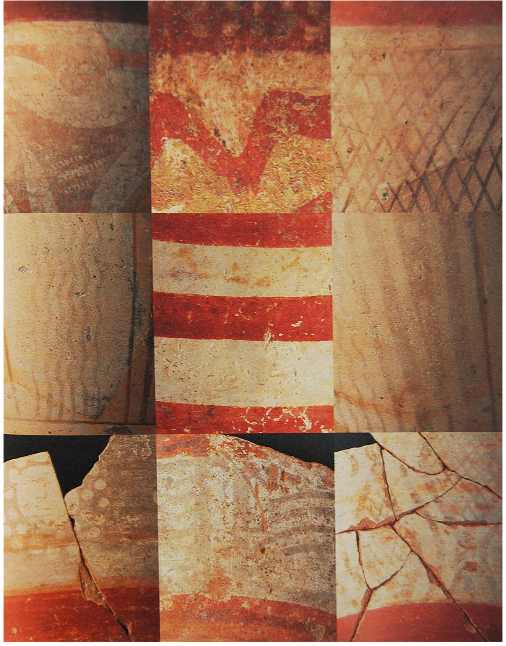

Figure 1: *Celtic fine-ceramic sherds with white colour application from about 100 years B.C. [2].*

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THE MONITORING OF INDOOR MUSEUM ENVIRONMENTS AND THE IMPACT OF THEIR CORROSIVITY ON COMPLEX ORGANIC MATERIALS

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Introduction

The aim of this paper is to report on the monitoring of indoor microclimates using dosimeters based on the quartz crystal microbalance principle and coated with (1) natural varnishes and (2) lead. The latter coating was used to detect the presence of volatile organic acids (VOCs) in organ pipes and microclimate frames containing paintings.

Experimental

In the MIMIC project (Microclimate Indoor Monitoring for Cultural Heritage), arrays of varnish coated crystals were exposed in holders in museums where the microclimate was monitored for periods of over a year in terms of RH,T, light, and externally generated pollutants [1]. The crystal dosimeters were coated with resin mastic varnish. The rationale for selection of this coating is described elsewhere [2]. Towards the end of the project continuous monitoring modules were prepared. Within the later SENSORGAN (Sensor System for Detection of Harmful Environments for Pipe Organs) and PROPAINT “Improved Protection of Paintings during Exhibition, Storage and Transit” projects the crystal holders were miniaturised and their controlling systems adapted for use within the organ pipes and microclimate frames containing paintings. In PROPAINT dammar and synthetic resins MS2A and B72 were also used. In current systems telemetric transfer of data has also been achieved. The new holders house 3 crystals. Lead coated crystals were exposed together with lead coupons and varnish coated crystals were exposed with varnish coated steel strips. Recently it has been shown that it is possible to rank the museum storage environments and archives with regard to corrosivity by exposing lead coupons [3].

Results and Conclusions

Damage assessment was based on the frequency shift of crystals and related to values obtained from accelerated ageing tests. Surface chemical changes were studied using X-ray Photoelectron Spectroscopy. In the MIMIC project sites where light levels were not controlled or where NO_2 levels were higher than expected showed most damage and chemical alteration to the varnish coating. In the SENSORGAN project testing was performed within the organ pipes in St.Botolph without Aldgate. It was found that when data were compared with laboratory calibration it was found that microclimate conditions were not posing a threat to the pipes. Within the PROPAINT project microclimate frames in five different museums showed that for the lead coated crystals and the lead coupons the change within the frame was always greater than outside the frame. Values obtained were commensurate with levels of acetic acid measured in these frames using passive samplers. Varnish coated crystals on the other hand gave a low response within the frames as their sensitivity was found to be to the presence of light and oxidising agents.

Acknowledgements

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THE USE OF NEAR INFRARED SPECTROSCOPY TO CHARACTERISE THE STATE OF HISTORIC SILKS

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Introduction

Silk is a culturally important textile, found in many artefacts of historic significance including clothing, furnishings, banners and decorations. However it is prone to deterioration via a variety of mechanisms, and this may be exacerbated by certain historically common treatments, such as bleaching and weighting. It is important to be able to accurately characterise both the condition and the processing of the material in order to inform strategies for conservation, display and storage, as well as more fully appreciating the history of the artefact. Near infrared (NIR) spectroscopy allows rapid, non-invasive, *in situ* analysis. When combined with chemometrics, correlations may be drawn between spectra and other data, such as markers of deterioration like tenacity, providing a strong predictive tool. Using this approach, we have demonstrated that it is possible to gain information about the state of deterioration of silk, regardless of the exact degradation pathway, as well as treatments such as metal salt weighting. NIR spectroscopy minimises unnecessary interference with an artefact, and highlights those objects which may warrant additional investigation via other more expensive, time-consuming or invasive methods.

Experimental

Silk samples prepared via historically accurate processing methods followed by artificial ageing, along with a collection of historic silk samples between 50 and 200 years old, were assessed by NIR spectroscopy (*Perkin-Elmer 'Spectrum One NTS'* with fibre optic probe) and mechanical testing (*Instron '5544'*). Correlations between the data were derived using chemometric analysis (*Camo Technologies 'Unscrambler, v9.7'*). These models were then used to predict the condition of a number of historic silk artefacts not previously investigated.

Results

A good correlation can be drawn between the NIR spectra and the tensile strength of the materials (Fig. 1). Using these spectra it is also possible to gain an indication of the weighting regimes which the fabrics have undergone (Fig. 2). The predictions based on these models were found to give a good indication of the state of the historic silk artefacts.

Conclusions

NIR spectroscopy is potentially a very powerful analytical method for cultural heritage collections, as it permits rapid, non-invasive investigations to be carried out, and can be performed on artefacts on display or in storage with the minimum of intervention or handling. We have demonstrated that when used in combination with chemometric analysis, it is possible to characterise various important properties of silk artefacts, which will not only allow the most appropriate conservation strategies to be chosen, but also give a greater appreciation of the history and origins of the object.

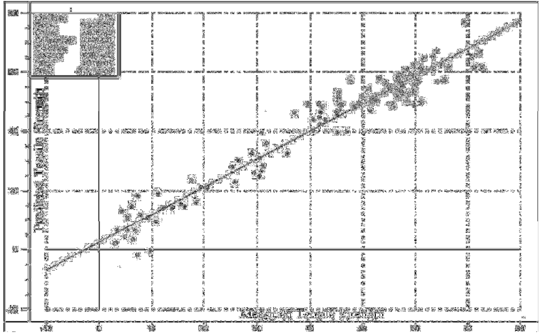

Figure 1: *Correlation between actual and predicted strength, based on NIR/chemometic models.*

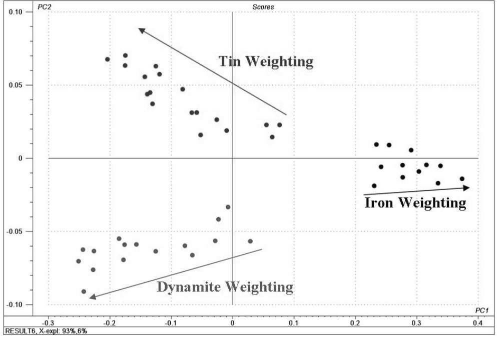

Figure 2: *Characterisation of different weighting regimes, based on NIR/chemometic models.*

Acknowledgements

The authors would like to thank Nell Hoare (Director of the TCC) and their colleagues for support and advice. The research was funded by the AHRC and the Korean Research Foundation.

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PRELIMINARY STUDY ON THE WOOD FROM AN ANCIENT ROMAN *ROSTRUM*

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Introduction

The conservation and restoration of complex artefacts present multidisciplinary problems related to the constituting materials, the degradation phenomena and its conservation.

This work presents a preliminary study on the wood part of an extremely rare Roman *rostrum* (a naval offensive element with the form of a bow) from a shipwreck, probably from Sextus Pompey’s fleet, found off Messina (Sicily, Italy). Data will be useful to assess the conservation state of the piece of art and give hints for the conservation treatment.

Experimental

Analysed samples came from a detached piece from the waterlogged *rostrum*. NMR measurements were carried out in solid phase by the cross polarization magic angle spinning, $^{13}C\ \{^1H\}$ CP-MAS, technique on wet and vacuum dehydrated samples. XRD and FTIR (in transmission mode) measurements were carried out on dry samples.

Results

The XRD pattern is shown in Fig. 1.

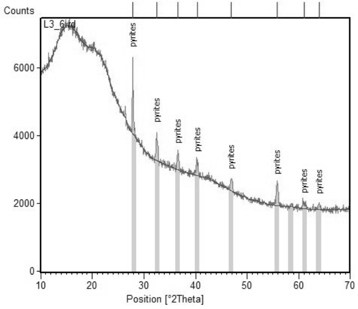

***Figure 1**: the XRD pattern*

Amorphous wide bands of cellulose centred at 15.1 and 20.3°2θ are well visible while peaks of the relative crystalline phase are absent. Remaining reflection peaks are referable to pyrite, FeS_2.

The FTIR spectrum is shown in Fig. 2. It contains a strong peak referable to lignin, 1509cm^{-1}. A peak of the carbonyl group (between 1735 and 1750cm^{-1}) is absent. Both are evidences for a major degradation of cellulose matrix.

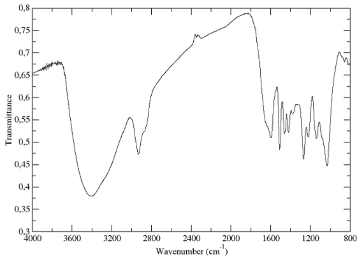

***Figure 2**: the FTIR spectrum*

Fig. 3. is the $^{13}C\ \{^1H\}$ CP-MAS NMR spectrum.

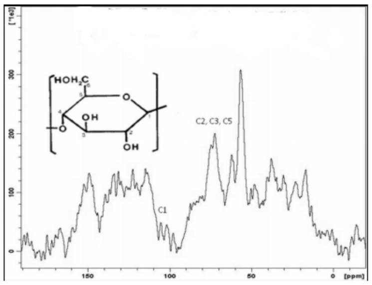

***Figure 3**: the $^{13}C\ \{^1H\}$ CP-MAS NMR spectrum*

The complex signal at about 72 ppm evidences a low cellulose residue. Peaks owed to lignin network range from 0 to 70ppm, for aliphatic parts, and from 105 to 170ppm, for aromatic ones.

Conclusions

The presented preliminary investigation of an ancient Roman *rostrum* assessed the bad conservation state of cellulose part of the wood. The XRD pattern interpretation inferred the presence of FeS_2 which can lead to a massive decomposition of the artefact caused by the oxidation in wet environment. Further analyses, such as Raman and XPS, are needed. The whole investigation will serve as a basis for evaluate possible conservation treatments based on the use of nanostructured materials (e.g. $Ca(OH)_2$, carbon nanotubes) and/or polymers (e.g. PEG).

Acknowledgements

Prof. V. Turco Liveri and Dr. A.M. Ruggirello are kindly acknowledged for FTIR measurements.

EDXRF AND FTIR COMBINED STUDIES OF ARCHAEOLOGICAL ARTWORKS IN CRETE

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Introduction

Energy Dispersive X-ray Fluorescence (EDXRF) and Fourier Transform Infrared spectroscopy (FTIR) can be used as complementary techniques for the characterization of various archaeological artworks. In particular EDXRF and FTIR: (a) identified pigments decorated Hellenistic figurines, (b) characterized Late Minoan (1400-1200 B.C.) metallic finds, (c) analyzed mortars and plasters from Minoan up to Turkish domination period and finally assessed the efficiency of stone consolidation agents.

Experimental

EDXRF was employed for the identification of blue, black, white and purple-pigmented areas decorated Hellenistic figurines, excavated from a rock-cut tomb in the archaeological zone of Chania, Crete, Greece. FTIR and X-ray diffraction analysis (XRD) gave complementary information on the composition of pigments. EDXRF and FTIR characterized Late Minoan (1400-1200 B.C.) metallic finds excavated from tombs of the Late Minoan cemetery, at Armenoi, Rethymnon, Crete.

Limestones from the Cathedral of Chania treated with barium hydroxide 20 years ago, as well as porous bioclastic limestones of small pore radii (~2.5 μm) and sandy limestones of large pore radii (~57 μm) treated with silicon-based strengthening products (tetraethoxysilane, elastified silicic acid ethyl ester, an aqueous colloidal dispersion of silica particles and an oligomeric siloxane water repellent) were assessed by EDXRF, in order to identify the penetration depth of Ba and Si. EDXRF was employed for qualitative and quantitative analyses of the mortars and plasters. FTIR spectroscopy was performed in the binders of the studied mortars to distinguish overlapping compounds present in low quantity in the total mortar. Portable EDXRF was also used to detect the constituent elements of construction materials in monuments.

Results

Precious pigments, such as Egyptian blue for the bluish areas, Tyrian purple for the purple ones, and the rare huntite for the white-pigmented areas were identified [1]. The results obtained by EDXRF, such as the Copper and Bromine detection in the blue and purple-pigmented areas, respectively, assisted in the identification of Egyptian blue and Tyrian purple by FTIR. The analyzed metallic objects consisted of copper, tin, argent, lead and iron. More specifically, one of the three rings consisted exclusively of silver, while the other two consisted of copper mixed with tin. The analysis of two nails revealed copper as the main constituent with minor amounts of tin, lead and iron. An interesting finding referred to the identification of pure tin in a small bead and other metallic fragments.

EDXRF indicated that the silicon-based consolidation products reached a depth from the surface of 30 mm and were evenly distributed inside the stone, except for the aqueous colloidal dispersion of silica particles, which accumulated up to the first 10 mm from the surface [2]. As far as barium hydroxide treatment efficiency is concerned, barium was detected on the surface of the treated stones only by means of EDXRF, whereas FTIR shows no signs of barium compounds. EDXRF analysis reveals that barium is sporadically present on the treated surface with a depth distribution of up to 2 mm [3].

The analyses of mortars and plasters enabled their characterization and classification into aerial lime and hydraulic-lime mortars and gave indications on the raw materials employed and the production technology.

Conclusions

The EDXRF and FTIR identification of the above mentioned pigments and metals in the archaeological objects, as well as the mortar characterization provided invaluable information on the technological aspects of their production period. Furthermore, cultural exchanges were also indicated, since the pigment huntite and the tin objects cannot be related to local resources. In the case of treatment assessment the penetration depth of Si and Ba is strongly correlated with the treatment efficiency. Therefore, EDXRF and FTIR are powerful tools for archaeometrical and conservation applications.

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THE IAEA ACTIVITIES RELATED TO APPLICATIONS OF NUCLEAR ANALYTICAL TECHNIQUES FOR CHARACTERIZATION AND PROTECTION OF CULTURAL HERITAGE OBJECTS

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Introduction

XRF is an analytical technique which is particularly suitable for development of portable instruments and in-situ analytical methodologies. The IAEA supports applications of his techniques through coordination of research in the field of in situ characterization of cultural heritage (CH) objects under the co-called coordinated research projects (CRPs) as well as establishing adequate infrastructure and development of skilled personnel under Technical Cooperation (TC) projects. These activities are supplemented by the efforts of the IAEA Laboratories at Seibersdorf involved in the development of portable XRF spectrometers for in situ analysis of CH objects [1]. The paper presents the recent results and selected applications of portable XRF spectrometers.

Experimental

A development of portable XRF spectrometers and associated in situ analytical methodologies requires optimization of the geometry and excitation-detection conditions as well as a careful consideration of the interfering effects which affect the accuracy of the analytical results [2]. In order to extend applicability range of the portable XRF system a vacuum chamber, poly-capillary lens and an SDD detector were applied.

Results

A recently concluded CRP on applications of nuclear analytical techniques to investigate the authenticity of art objects resulted in the methods and procedures for analysis of art and archaeological artefacts as well as databases which can be used for identification of provenance, age and confirmation of authenticity of the CH objects. A regional TC project on nuclear techniques for protection of CH artefacts in the Mediterranean region was focused on applications of XRF and ion beam analysis for characterization of CH objects in support of documentation and conservation, use of gamma radiation for preservation, and dating techniques. The portable XRF spectrometer (see Fig.1) designed and constructed in cooperation with the Atomic Institute (ATI) of the Austrian Universities [3] includes a compact vacuum chamber, a 50 W low-power palladium anode X-ray tube, a poly-capillary lens (beam spot size of 200 μm) and collimator (1 mm), and an SDD detector. The detection limits for the measurement time of 1500 s, were in the range from 25 – 620 ppm for Ti and Al, respectively. A fundamental parameter method was used for quantification. The portable XRF system was applied by the Museum of Fine Arts in Vienna for characterization of various CH objects including bronzes, paintings, papers and glasses [1].

Conclusions

The IAEA provides support in applications of nuclear analytical techniques in the field of CH through various complementary modalities including CRPs, TC projects, training and development of prototype instruments. The beneficiaries are the XRF laboratories in both developing and developed Member States.

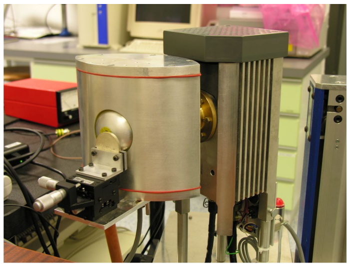

Figure 1: *Portable XRF spectrometer*

Acknowledgements

We are grateful for collaboration and contribution of Prof. P. Wobrauschek, Prof. C. Streli, Dr. G. Buzanich, Dr. M. Griesser and Dr. K. Uhlir.

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QUANTITATIVE X-RAY FLUORESCENCE ANALYSE OF AN EGYPTIAN FAIENCE PENDANT AND COMPARISON WITH PIXE

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Introduction

The non-destructive characterization of archaeological artefacts and art objects are considered to be among the most important and popular interdisciplinary applications of beam analysis techniques. The particle induced X-ray emission technique (PIXE) provides the elemental quantitative composition of any kind of material with great sensitivity. The X-ray fluorescence (XRF) technique is a popular choice in the archaeometric field for in situ investigations with portable instruments. This normally enables qualitative and semi-quantitative information retrieval from the objects of interest. Thanks to the program PyMca [1] developed at the European Synchrotron Radiation Facility analysis with portable systems have improved noticeably. The main objective of this work is to show the performance of this new software, which we have implemented in two XRF portable systems with different anodes, and the comparison with PIXE results in the analysis of an Egyptian faience pendant.

Experimental

The analyzed object was a yellow faience pendant, dated 1350 b.C. (XVIIIth Egyptian dinasty). PIXE measurements were performed with the external microprobe set-up of the AGLAE facility [2], and data treatment with GUPIX program. Two XRF portable systems have been designed and constructed in the C2RMF lab. One of them uses a X-ray tube with Ag anode, a straight monocapillary lens and a solid state Si(Li) AXAS-V detector. This system includes helium for detecting elements down to sodium. The other system with Cu anode is fully described by Gianoncelli et al [3]. X-ray spectra in both systems were analyzed by the dedicated software PyMca, based on the Fundamental Parameter Method.

Results

The values obtained by XRF portable systems using PyMca are very similar between them and to those obtained by PIXE, as shown in Figure 1. The accurate knowledge of the emission spectrum energy distribution in both portable systems and excellent internal calibration have allowed these results. In the case of the Ag anode apparatus, the highest differences are found in the elements with low Z. In the case of the other portable system, with Cu anode, the measurements were performed in air, so the correct analysis of elements of low energy (Z<17) was not possible.

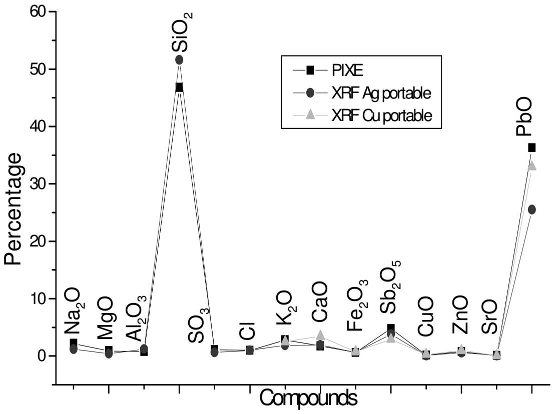

Figure 1: *Comparison of quantitative results obtained by PIXE and XRF portable systems*

Conclusions

PyMca implements most of the needs of X-ray fluorescence spectroscopy. This work shows that XRF portable systems can be used for doing quantitative analysis using it, obtaining a similar accuracy to that obtained with other techniques such as PIXE. The comparison between PIXE and XRF results shows very similar results in the case of the analyzed Egyptian piece.

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NOVEL EXTENTIONS OF PULSED RAMAN AND LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) IN ART CONSERVATION

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Introduction

A nanosecond pulsed laser setup has been optimized to perform Laser Induced Breakdown Spectroscopy (LIBS) and Pulsed Raman Spectroscopy [1] measurements of samples from works of art. No specific sample preparation was required before the measurements and no visual or structural damage was observed. Depth profiling using LIBS was performed in one of the samples, providing elemental information along the different layers composing the object and covering its surface. Furthermore, improvements in instrumentation may allow the discrimination between Raman and luminescence phenomena on the basis of their different temporal responses using Time Resolved Raman Spectroscopy. By using an Intensified CCD camera synchronised with the laser pulse, it becomes possible to apply a very short temporal gate in order to record the entire Raman signal and completely avoid contributions from luminescence.

Experimental

Various objects representative of different artistic techniques, were chosen and have different provenances and also present distinct states of conservation. A fragment of a wall painting from the "Assunta" church in Savigliano (Cuneo, Italy), a fragment of a ceramic decorative tile from building in Yemen and areas of a bronze head belonging to the "Porta del Paradiso" (Gate of Heaven) of the Florence Baptistery have been analysed as part of this work. This diversity in the choice of samples was intentional and served to test the instrument's capabilities and versatility. Furthermore, an alternative method for the identification of natural and synthetic ultramarine have been discussed [2]. Measurements were performed directly on the samples/objects without sample preparation. Pulsed Raman acquisition was also carried out on a crystal of ruby in order to study fluorescence elimination.

Results

Pulsed Raman and LIBS spectra (fig.1) of the samples were acquired with the laser emitting at 532 nm. The use of a pulsed source coupled with an intensified and gated detector allowed the full removal of contributions from environmental light [3]. The delay and gate times have been optimized in order to enhance the Raman signal against luminescence, with significant advantages for the analysis of samples in ambient lighting conditions. The results from the two techniques allowed the identification of the original materials and contamination products.

Conclusions

The quality of the results and the rather short time needed for the measurements and for switching between techniques confirmed the instrument's capabilities and specificity for the analysis of samples from works of art. Potential improvements and future work will be discussed,

Fresco depicting scenes of the Virgin Mary and her following Assumption.

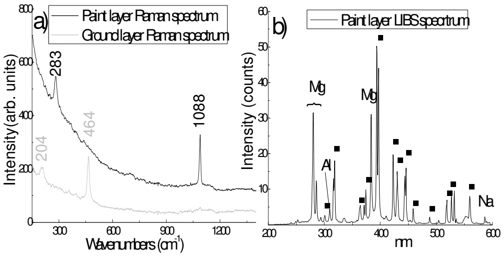

Figure 1: *a) Raman spectra acquired on the pigmented area (black) and on the ground layer (grey), respectively. b) LIBS spectrum acquired on the pigmented area. The spectrum has been acquired with single laser shot.*

Acknowledgements

We would like to thank "Ente Cassa di Risparmio di Firenze" for the financial support and the restorer Andrea Vigna for helping in providing fresco samples.

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O35

A NOVEL PORTABLE XRF SPECTROMETER: FIRST APPLICATION TO A GILDED BRONZE FROM THE FLORENCE BAPTISTERY

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Introduction

The sculpture group of the "Porta del Paradiso (Gate of Paradise)", the eastern door of the Florence Baptistery realised by Lorenzo Ghiberti in XV century, is one of the most representative and superb creations of the Florentine Renaissance. It is composed of ten gilded bronze panels surrounded by frames made of gilded bronze as well. All the parts of the door have been submitted to a long and difficult restoration at the conservation institute Opificio delle Pietre Dure in Florence. Different scientific techniques have also been used to characterise materials and to monitor the different phases of the cleaning.

We analysed one of the "Prophet heads" belonging to the frame with the new portable XRF spectrometer that we built up at LABEC laboratory of INFN-Florence, in collaboration with the ICVBC institute of CNR. The intent was to determine the composition of the bronze bulk and that of the gilding. Furthermore, we were asked to compare the results obtained in zones where different cleaning procedures had been used.

Experimental

The instrument used presents some innovative features. The primary X radiation is produced by two tubes (not used simultaneously) placed at different angles with respect to the detector axis and with different anodes (Mo and Ti). The efficiency in producing characteristic X-rays from the target material is thus optimised for a broader range of energies. Furthermore, the instrument is also provided with a Helium flow in front of both the tubes and the detector, thus giving the possibility to produce and detect even low energy X-rays, down to 1 keV.

Results

Several measurements were performed on the sculpture in different types of areas. The spectra obtained were analysed by the AXIL software package, for both fitting procedure and quantitative analysis. The composition of the bronze bulk was deduced by analyses performed on cleaned zones of the back, where obviously no gilding is present. The composition and thickness of the gilding layer was then obtained from spectra taken in different zones of the front face of the sculpture. Also an uncleaned zone was analysed in order to detect – by comparison with the others – deposition or alteration processes.

Conclusions

The gilded bronze sculpture analysed was characterised by a fully non-invasive technique. The new custom-realised spectrometer demonstrated the advantages of using two tubes and the necessity of the helium flow, even for a metallic sample, when light elements due to alteration and deposition processes have to be identified. Results are being compared with those obtained with different techniques, such as LIBS and Raman spectroscopy [1].

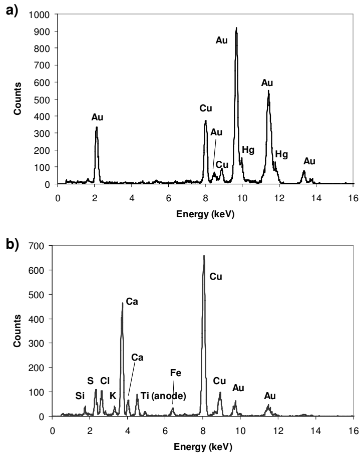

Figure 1: *Examples of spectra collected with the two tubes: (a) a cleaned gilded bronze area, using the Mo anode tube; (b) an uncleaned area with the Ti anode tube.*

Acknowledgements

The authors would like to thank Simone Porcinai and Andrea Cagnini from Opificio delle Pietre Dure in Florence. The instrument has been developed thanks to the contribution of Ente Cassa di Risparmio di Firenze.

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MACROMOLECULES IN ART AND ARCHAEOLOGY

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Since ancient times, a wide variety of natural organic materials have been used as adhesives, sealants, painting and coating materials. Proteins, oils, gums, natural resins and resinous materials played a prominent role, since their intrinsic properties meant that they could be used not only as painting materials, adhesives, hydro-repellents, coating and sealing agents, but also as flavours, incense, ingredients for cosmetics, medicines and mummification balms. Heating processes applied to these materials have deeply modified the chemical composition of the original ones, inducing aromatisation, demethylation and decarboxilation reactions with formation of new species, generally having lower chemical weight.

The chemical characterization of such organic materials when properly integrated with related information from historical sources and archaeological data, has in the last few years considerably improved our knowledge of painting techniques, the crafts and technologies of the past, and has provided art historians and archaeologists with vital information. In fact, identifying specific materials from molecular patterns can assist in assessing the role that these substances played and in determining the use of artefacts on which these residues survive.

The study of organic materials in art and archaeology is a challenge due not only to the complexity of the chemical composition of the natural substances that may be present alone and in mixtures, but also to changes in the chemical composition as a consequence of human activities such as cooking, heating, or mixing materials in order to modify their properties in view of a specific use. Moreover, degradation due to ageing under the influence of different.

This lecture reviews the most significant results obtained worldwide by the application of analytical procedures mainly based on mass spectrometric techniques [1,2] to painting and archaeological samples. It highlights the presence of stable macromolecules, permitting a critical interpretation and evaluation of the obtained results. Basically, the identification of materials is based on both molecular fingerprint and the presence of one or more specific molecular biomarkers which have survived ageing or which are formed over the centuries as stable products of ageing processes.

Case studies on the chemical characterization of paintings, of organic residues in ointment jars and of ancient resinous jewelers will be presented.

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FROM EGG TEMPERA TO OIL ON CANVAS: ANALYTICAL STUDY OF THE EVOLUTION OF THE POST-BYZANTINE TECHNIQUE

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Introduction

Specific artistic styles are characterised by painting techniques developed as a result of different influences from various sources. The post Byzantine style represents the ''modernisation'' of Greek art from the early current trends of egg tempera on panel painting with the move to oil on canvas.

This paper focuses on the analytical study of art work of the period in order to track how styles changed through the adoption of different materials in current use in Europe.

Experimental

This study was based on the analysis of samples taken from 121 panel painting which were examples of the work of the most important artists who contributed to the evolution of Greek art between the 16th and 19th centuries. Materials were characterised using a multi-method approach. Elemental composition was determined by Energy Dispersive X-ray Analysis, whereas the binders, ground etc were investigated using Fourier Transform Infrared Microscopy and Gas Chromatography. Raman microscopy and staining of cross-sections were used to offer complementary information wherever necessary.

Results

The chemical nature of the pigments was identified and the identification of the separate occurrences of emulsions and pure oils on different art works indicated that the changes in technique that took place in the post Byzantine period could be tracked from the samples investigated. The dates attributed to the artists plus the chemical analysis allowed the progress of these changes to be monitored versus time.

Conclusion

One of the aims of this project was to investigate the nature of the binding media used by the post-Byzantine painters from Crete and the islands of Ionion and to relate observed changes to possible Western influences. The change of the painting characteristics exemplifies the extent of those influences and scientific analysis allows us to recreate the artist's palette. This approach produced a more complete idea of this transitional period from which the artists proceeded to secular oil painting.

It is obvious that while in the Byzantine art the main binder was egg yolk, immediately after the creation of the post-Byzantine School egg/oil emulsion and drying oils were introduced. In the 16th century there seems to be a rise in the use of drying oils, either in the form of an additive layer over a proteinaceous one or in the form of a single layer binder. The 17th century established the use of emulsions, until the 18th century where the use of drying oils prevails. This unexpected sequence of changes was repeated through all the schools studied, it seems reproducible through each series of samples and is not being influenced by other considerations.

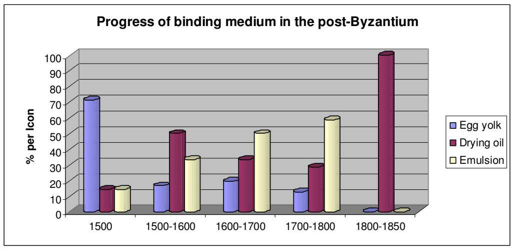

Figure 1: *Chart showing the evolution of the painting technique through the post-Byzantium*

Acknowledgements

This work was carried out at De Montfort University, United Kingdomand the National Gallery of Greece. Thanks are due to Dr M. Doulgeridis (NG), Panagiotis Asimakopoulos (Perkin Elmer) for GC instruction and Dr P. Vandenabeele (University of Ghent) for the µRaman analysis of the paint samples.

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COLOURED GLAZES ON SILVER LEAF: IDENTIFICATION OF THE PROTEIN MEDIA USED IN THE GROUNDS AND COATINGS

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Introduction

Coloured glazes on metal leaf surfaces have been widely used by painters and polychromers to embellish works of art to give them meaning and optical dynamism [1]. In German-speaking countries, this technique is known as 'Lüster' or 'Lüstrierung', a term derived from the Latin word *lustrare*, which means 'to brighten'. These delicate and technically sophisticated coatings create bright luminous colours caused by the reflection of the light transmitted through the glaze from the metallic surface underneath. In the seventeenth and eighteenth centuries the uses of coloured glazes in Central Europe reached new heights and were applied on a much larger scale especially in connection with the imitation of precious materials. Often this technique – which is actually a combination of techniques – revealed an unforeseen complexity due to the multi-layered build-up and the use of various material mixtures, including a broad spectrum of colourants, binding media, metals, and additives. In this entire complex proteinaceous binding media often played an important role especially in the ground and preparatory layers as well as ultra-thin intermediate coatings applied directly onto the metal leaf underneath the actual coloured glaze. In order to find out more about the type of protein used in historical samples, we develop an adapted proteomic-methodology on polychromy reconstructions.

Experimental

The analysed samples were taken from various reconstructions of coloured glazes and transparent coatings on silver leaf carried out between 2001 and 2008. The organic material used in model polychromy samples is animal glue, ox bile and egg white. Starting from the approximately 200 µg of reconstituted polychromy, proteins were extracted with an acidified solution with 1% trifluoroacetic acid using a grinding resin and additional ultrasonic steps [2,3]. The enzymatically hydrolyzed protein extract was analyzed by nanoLC nanoESI-Qh-FT-ICR MS/MS with an adapted chromatographic run for the low sample quantity (capillary column Pepmap C18, 75 µ i.d., 15 cm length, 3h gradient).

Results

The developed analytical methodology was evaluated on different types of binders, as for example skin rabbit glue, skin jack-rabbit glue, fish glue or Salianski fish glue, highlighting protein identification but also species identification using specific peptides. Relating to polychromy samples, the difficulty is increased as protein staining experiments using SYPRO Ruby fluorophore confirm that proteins are present in different layers, i.e. in ground which lies on the support and in coating which lies on the metal leaf. Consequently, a manual separation of the protein media was investigated; additionally several tests based on PALM microdissection were also evaluated. The application of the developed analytical methodology on these protein media highlights some identification promising results for the analysis of ancient polychromy.

Acknowledgements

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PARCHMENT CHARACTERIZATION AND DETERIORATION ASSESSMENT USING OPTICAL METHODS

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Introduction

Parchments are of considerable archeological importance. They consist of collagen matrix, possessing the basic triple helix structure of polypeptide chains.

Parchments are subjected to various deterioration processes, caused by a combination of humidity, light, temperature and microorganisms. Scientifically sound methods for estimating the actual condition of parchments are of considerable importance. Such tools are relevant to preservation control and to restoration. Various analytical techniques have been applied to parchments; however, new rapid methods for qualitative and quantitative identification and characterization are still needed. Obviously, such methods should be based on optical techniques.

In this study we propose the application of several optical methods:
(1) Native fluorescence,
(2) Synchronous fluorescence (SF),
(3) Laser induced breakdown spectroscopy (LIBS)
(4) Laser assisted depth profiling.

We examine the possibility of utilizing the obtained data for characterization of parchment condition and for assessment of their actual deterioration stage.

Experimental

Our parchment set consisted of 54 articles (37 modern, 17 historical), produced from different animal skins and found at different stages of deterioration.

Two deterioration procedures were performed: (a) harsh deterioration that results in full scale modification in the spectral variables, and (b) gentle deterioration that only slightly modifies the spectral characteristics, corresponding to the fist stages of the natural aging process. Both UV radiation and heating were applied, according to standard procedures.

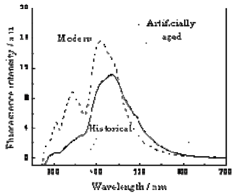
Surface synchronous fluorescence spectra were acquired using Aminco-Bowman spectrofluorimeter, equipped with front surface accessory. Laser ablation was performed for depth profiling, using a series of ongoing laser shots (Nd:YAG laser, 1064 nm, 7ns pulses, 1Hz). The same laser was used for LIBS measurements, where the spectra were acquired using an ICCD camera.

Results

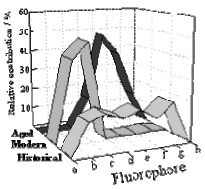
Parchment native fluorescence and its synchronous fluorescence were correlated to its aging or deterioration condition. Aging causes a fluorescence intensity drop, a spectral shift in the main emission peak and an overall change in the fluorescence spectral features. The discrimination of parchment samples into groups (modern, historical and artificially aged) was successfully performed.

Microscopic LIBS analysis provided local elemental speciation in parchments of various sources. Fast distinction between modern and historical samples, based on discriminant analysis of the LIBS data, was obtained. Animal type recognition was also possible based on Mg/Cu emission peak ratio.

Laser assisted depth profiling allowed for performing both elemental speciation and synchronous fluorescence measurements as a function of the depth. The data indicate that the parchment has layered structure and the dominant fluorophore in the upper layer is different from those in the lower layers. Moreover, layer resolved profiling allows for quantifying the contribution of each chromophore in each given layer to the measured SF spectra.



SF spectra of modern, historical and full artificially aged parchments.



Relative contribution of fluorophores in modern, ancient and artificially aged parchment samples

Conclusions

The proposed optical method qualifies well for fast parchment characterization and assessment of its deterioration stage.

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COMPARISON OF EXTRACTION METHODS FOR THE ANALYSIS OF NATURAL DYES IN HISTORICAL TEXTILES BY HPLC

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Introduction

Identification of colourants contained in historical textiles elucidates the history of the dyeing technology, is necessary for the documentation of the artworks, may be decisive for the development of effective and appropriate conservation strategies and is a challenging task for analytical chemists. Prior to HPLC analysis, textile samples have to be treated to extract and solubilise the contained dyestuffs. The sample preparation procedure is apparently of great importance as it can have enormous effects on the analytical results collected by HPLC. Despite its importance, the extraction of dyes from textile fibres has not been investigated in detail [1-3]. Treatment of the dyed fibres with methanolic HCl at elevated temperatures, suggested several years ago [4], is still the most widely adopted method. However, the use of HCl for the extraction of flavonoid dyes is disadvantageous, because most of the flavonoid dye components are sugar derivatives (glycosides) which under harsh acidic conditions are decomposed to their parent aglycons. Thus information of the materials used originally during the dyeing process of a historical textile may be lost. A similar disadvantage of the HCl method applies on the extraction of anthraquinone dyes [5]. Furthermore, polymethine dyes (e.g. turmeric), are degraded by HCl and therefore the widely adopted extraction method is not applicable on these dyes. The goal of the present study is to evaluate the efficiencies of four mild extraction methods and compare them with the standard HCl method.

Experimental

Wool fibres, used as reference samples, were dyed with *Dactylopius coccus Costa, Rubia tinctorum L., Isatis tinctoria L., Reseda luteola L., Curcuma longa L. and Cotinus coggygria SCOP.* The extraction yields of five extraction methods which include the use of HCl (typical extraction method), citric acid, oxalic acid, TFA and a combination of HCOOH and EDTA were evaluated for the following compounds: indigotin, indirubin curcumin, demethoxycurcumin, bisdemethoxy-curcumin, fisetin, sulfuretin, luteolin, luteolin-7-O-glucoside, apigenin, carminic acid, alizarin, puruprin and rubiadin. Extraction efficiencies of the five methods were compared on the basis of the (i) number, (ii) relative quantities and (iii) signal-to-noise ratios (S/N), of the compounds extracted from the wool substrates. HPLC-PDA-MS (Thermoquest, IK) was used for identification purposes and the aforementioned measurements.

Results

The results obtained for each of the three criteria are summarized as follows. (i) Flavonoid glycosides and curcuminoids are extracted with all methods except for the HCl method. (ii) Except for fisetin, apigenin, luteolin and luteolin-7-*O*-glucoside, elevated quantities of the other colouring compounds are extracted from wool fibres with the TFA method. (iii) High S/N ratios are recorded with the TFA extraction method. This was observed for all compounds except for luteolin-7-*O*-glucoside (the citric acid method gave better results than the TFA method) and fisetin (the oxalic acid method gave better results).

Conclusions

Although the assessment of a single extraction method which provides the best results for all tested dyes is very difficult, the results suggest that the TFA method is overal superior than the other extraction methods. For the first time it was shown that the evaluation of a dye extraction method from tecxtile substrates should inlcude S/N measurements; these were not reported by previous investigations [1-3].

Acknowledgements

This work was funded by the Greek Ministry of Development (GSRT) and the European Social Fund (EU) through the research program PENED2003 (No 03EΔ697).

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THE NEW VERSION OF THE PORTABLE XRD SYSTEM OF THE LANDIS LABORATORY AND ITS APPLICATION FOR THE NON-DESTRUCTIVE CHARACTERIZATION OF ANCIENT PIGMENTS

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Introduction

It is well known that the XRD technique can be applied for the mineralogical characterization of materials in the Cultural Heritage field.

Generally the XRD technique is applied with non-transportable instruments, so limiting its field of application only to small dimension objects or requiring a destructive sampling in order to analyze artifacts which can not be transferred to the laboratories of analysis.

In the last years many efforts have been dedicated to the development of portable systems, even if some limitation in terms of angular resolution or measurements time are often observed [1,2,3].

In this work the upgrade of a commercial portable XRD system, previously installed at the LANDIS laboratory of the LNS-INFN of Catania (Italy) for in-situ applications in the Cultural Heritage field, is presented [2].

The final version of the portable XRD system was used for the non-destructive mineralogical characterization of pigments. In particular its application, in combination with the portable PIXE technique developed at the LANDIS laboratory, for the quantitative characterization of Roman frescoes, is reported and discussed [4].

Experimental

A commercial portable XRD system, realized by the Italian ASSING company, was initially installed at the LANDIS laboratory. The system, based on a goniometric theta-theta geometry, was equipped with a Fe anode x-ray tube as source and with a Peltier cooled Si-PIN detector for collecting the x-rays diffracted by the investigated samples. Such a XRD system presents some important analytical capabilities: the sample can be positioned outside the goniometric circle allowing non-destructive measurements of non-movable artifacts (for examples wall paintings or frescoes); it allows the simultaneous XRD and XRF measurements on the same area of the sample; the selection of the x-ray energy used to perform the diffraction on samples is obtained by a digital filter that operates in the MCA analyzer of the detector; finally it presents compact dimensions and low weight and it is easily transportable in-situ.

However, this commercial system evidenced some analytical limitations: it was necessary to operate long time measurements (more than 3 hours) in order to get enough statistics in the collected XRD spectra and it presented a low angular resolution reducing the capabilities to resolve peaks with close diffraction angles.

An upgraded version of the commercial XRD system was realized by the LANDIS group. In particular a new x-ray source, based on a low power microfocus tube coupled with a polycapillary semi-lens, has been studied and installed on the diffractometer. The use of such a modular component enabled the possibility to use high intensity parallel x-ray beams for XRD investigation. The improvements of the new experimental set-up of the system compared with the previous commercial version are about 30-40% for angular resolution and about 4-5 times higher for the beam intensity.

Results

The new version of the diffractometer was applied for the non-destructive characterization of pigments present in some Roman frescoes.

Moreover the combination of the XRD technique and of the PIXE method, both performed with the portable instruments of the LANDIS laboratory, allowed to get even quantitative information about the mixture of pigments used to realize the wall paintings.

Conclusions

The use of microfocus x-ray tube and polycapillary optics allows to design a new version of a portable XRD system with good performances concerning angular resolution and measurement time.

Finally it was shown how the use of the XRD technique in association with the PIXE method allows to obtain accurate quantitative results in the analysis of mixtures of ancient pigments.

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A PORTABLE, VACUUM-CHAMBER EQUIPPED XRF-INSTRUMENT, DESIGNED FOR THE SOPHISTICATED NEEDS OF THE KHM, VIENNA

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Introduction

For the study of the miscellaneous and valuable objects of the collections of the Kunsthistorisches Museum (KHM – with its affiliated institutions, the Museum of Ethnology Vienna [MVK] and the Austrian Theatre Museum [ÖTM]), in order to clarify their compositions and ways of production as well as to support conservation and restoration efforts, a non-destructive technique like x-ray fluorescence spectrometry (XRF) is required. In a co-operation of the Conservation Science Department of the KHM with the IAEA (International Atomic Energy Agency) and the ATI (Atomic Institute), a prototype XRF instrument developed by the IAEA and ATI was applied and tested at the museum. The portable focused-beam XRF spectrometer equipped with a compact vacuum chamber which houses the x-ray beam optics (polycapillary) and the detector head allows determination of chemical elements from sodium (Na) upwards [1]. In this way the palette of materials that can be analysed successfully has been expanded to materials like glass and enamels. Although several projects based on this instrument were performed successfully, a need for some improvements concerning the design and the detection limits for the light elements became evident. Therefore, within a research project founded by the Austrian Science Fund (FWF, project no. L430-N19; „Portable Art Analyzer – PART"), an enhanced portable XRF instrument has been designed, constructed and optimised to cope with the different analytical problems that arise in a wide-spread museum collection of miscellaneous objects.

Experimental

The development and construction of this XRF instrument was done through a co-operation of the above mentioned institutes. The new instrument meets all the mechanical requirements that come along with the widespread applications at the KHM, including analysis of Egyptian, Antique, Baroque and Renaissance artworks, paintings, historical musical instruments, textiles, coins, and arms and armours as well as highly valuable objects from the affiliated institutions. The major improvements are:

- Much more compact construction of the measuring head
- Several electronically controlled movable translation stages are included to allow exact positioning in front of the object.
- Improvements concerning the 8 µm Kapton®-window of the measuring head
- Modular design and modern components were applied.
- Possibility of using different x-ray tubes (Mo, Cr).
- Detachable measuring head.

Results

The results of the first measurements done for different standard materials and the analysis performed on museum objects will be presented.

Conclusions

The innovative XRF-instrument (Fig. 1) was designed to meet various requirements of the users of the Conservation Science Department. The first experiments confirmed usefulness and outstanding features of the portable spectrometer.

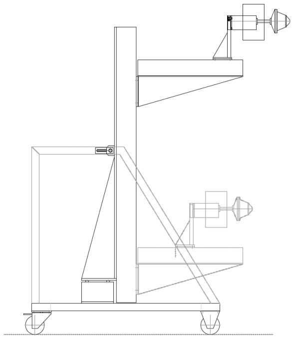

Figure 1: *Technical sketch of the innovative, newly designed portable XRF instrument.*

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A COMBINED USE OF FORS, XRF AND RAMAN SPECTROSCOPY IN THE STUDY OF MURAL PAINTINGS IN THE AOSTA VALLEY (ITALY)

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Introduction

Fibre optic reflectance spectroscopy (FORS), X-ray fluorescence (XRF) and Raman spectroscopy are among the most suitable non-destructive techniques for investigating pigments utilized in the execution of mural paintings. Taking advantage of the availability of portable equipments these techniques may be conveniently used for in situ investigation; this can allow one to proceed with selected sampling in view of a more detailed study by laboratory equipments, without destruction of the analytical samples.

Experimental

FORS, XRF and Raman spectroscopy were used for studying two mural paintings, which decorate the external façade and the internal apsidal wall of a chapel dedicated to St. Maxim and located at Challand St. Victor in the Aosta Valley (Italy). The paintings are attributed to Giacomino of Ivrea, a painter active around the mid fifteenth century. FORS and XRF analyses were performed in situ on selected areas of the paintings; 145 spectra were collected by FORS in the 400-1100 nm spectral region on both façade and apse; only the apsidal painting was studied by XRF, determining the composition of 52 spots. On the basis of the information obtained by in situ analysis, 23 samples were collected for examination under a stereomicroscope, and 17 of them were further studied by Raman spectroscopy. An Assing Lithos 3000 XRF spectrometer, a Zeiss Corona 45 Vis fibre optic reflectance spectrophotometer, and a Jobin-Yvon Labram Raman spectrometer were used for the analysis of the mural paintings.

Results

The obtained results point to the use of pigments such as calcite, azurite, malachite, vermilion, and red and yellow ochre. A particular situation has been put into evidence concerning the use of black pigments, since Raman spectroscopy points to the use of graphite rather than carbon obtained from wood; this may be related to the presence of graphite deposits in the Aosta Valley, even though not so close to the locality where the paintings were executed. Furthermore, evidence was gained of the presence of a layer of smalt superimposed to azurite in an area of the apse showing evidence of repainting; the use of smalt suggests that the painting was subjected to retouching at a relatively early stage after the original execution.

Conclusions

As a whole, the obtained results confirm the importance of the use of non-destructive techniques for in situ analysis of mural paintings, complemented by micro-destructive analysis of selected samples. In the present case, it has been possible to recognize pigments utilized in the course of the original execution and a subsequent retouching; furthermore, it has been put into evidence the use of locally available mineral pigments.

O44

MICRO-XRF AND LIBS ANALYSIS OF GILDED BRONZE FIGURINES AT THE NATIONAL ARCHAEOLOGICAL MUSEUM OF DAMASCUS

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Introduction

During the PROMET campaign in Syria, micro-XRF and LIBS examination of selected metal artefacts was performed [1]. This present work is focused on the analytical investigation of three unique gilded bronze figurines (Fig. 1), which belong to the late bronze age (1400-1300 B.C.) and were discovered at the Ugarite site. The Eail God (RS23) figurine has never been conserved and it presents a poor state of preservation covered by thick layers of green and black colored corrosion products. The other two gilded figurines (357 and S06), attributed to depict the Baal God, have been recently (2007) conserved with BTA and protected with the application of a wax coating. he analytical investigation aimed to characterize the composition and thickness of the gold leafs applied, the alloy composition and to identify the nature of the corrosion products and of the patina present on the artefacts surface (Fig.2).

Eail God RS23 *Baal God 357* *Baal God S06*

Figure 1: *The gilded bronze figurines analyzed at the Damascus Archaeological Museum*

Experimental

The mobile micro-XRF spectrometer is a customized design and development based on the Artax model (Bruker-AXS), whereas the LIBS one has been designed and developed in-house (see ref. [1] for details). For the quantification of the gold leafs, four reference gold alloys (Fischer) were used to provide calibration lines between relative intensity yield (Ag/Au, Cu/Au) and respective concentration ratios. The Ag-K/Ag-L intensity ratio served also to estimate a lower limit of the gold leaf's thickness. Measurements on copper reference alloys (BCR-691) defined quantitative criteria to assess suitability of data for quantification providing in some cases informative compositions.

Results-Discussion

The thickness of the gold leafs was estimated to be more than about 15 μm for all cases examined. The Ag and Cu maximum concentrations were not exceeded 15% and 4%, respectively. It is noted that the gold leaf(s) composition used to cover the front side of the Eail God is quite different than the one used in the back exhibiting remarkable purity (almost 96%). The raw metal of the three figurines is a typical bronze including very minor amounts of As, Zn and traces of Pb and Se. For the Baal God (357), a tin content of about 7% was estimated. Green areas are obviously associated with a Cu based corrosion product, possibly copper carbonate (malachite), due to the very minor and selective local presence of elements like S and Cl that form with Cu different corrosion products. Black areas are characterized either by the strong presence of Sn-L lines (possible due to the presence of cassiterite), or by a copper oxide layer that absorbs completely the low energy Sn-L characteristic X-rays.

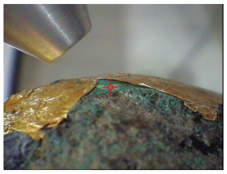

Figure 2: *Detail of an analyzed area on Eail God surface, presenting a green corrosion layer and details of the gold leaf applied.*

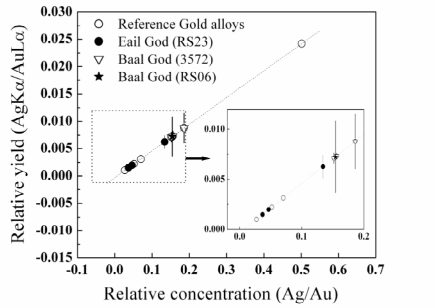

Figure 3*: Measured Ag/Au concentration for different gold leafs on the three figurines. Uncertainties represent st. dev. among individual micro-XRF measurements during areal-scans.*

Acknowledgements

This work was funded by the PROMET project, PROtection of METals, FP6-2002-INCO-MPC-1, www.promet.org.gr

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RELIABILITY OF OPTICAL MICROSCOPY, X-RAY DIFFRACTION AND X-RAY FLUORESCENCE FOR STUDYING TESSERAE FROM MOSSAICS

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Introduction

In Roman times ancient Kissamos, situated in the North West part of Crete (Greece), expanded and evolved in a modern town with many public buildings and urban villas. In an urban villa, the house of Pheidias, which was build in the 2nd – 3rd century AD, there is a beautiful mosaic which depicts drunken Dionyssos with two members of his thiasos and his sacred panther.

This paper discusses the diagnostic analysis using optical microscopy, X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) for the study of tesserae (fragments) from mosaics.

The study of the different mosaic tesserae is very important for their identification, especially in the case of natural stone fragments to locate the origin of the raw material.

Experimental

More than 50 tesserae were analysed covering macroscopically different materials and colors. Two different types of samples were distinguished, stone and glass tesserae. The dimension of the tesserae were 1x1cm up to 1x2 cm. Thin sections were prepared, from pieces not bigger than 5X5 mm, for the optical microscopy study using a polarizing microscope.

For the X-Ray diffraction analysis a powder diffractometer was used, equipped with a solid state detector, which allows high count rates and short measuring time. Two different techniques were applied: First, zero Background (Si) sample holders minimize the background and the sample amount, (<20mg) and second, direct measurements on the surface of the tesserae samples were applied. The quantitative analysis was carried out by the Rietveld Method (Hill, 1993).

XRF measurements were carried out only on the glass tesserae, using a micro-XRF spectrometer (Karydas, 2008).

Results

Based on the XRD measurements we distinguished the following groups:

1. Samples, which consist mainly of calcite with minor quantities of quartz. 2. Samples, which consist mainly of calcite with different quantities of dolomite and quartz. 3. Samples with high quartz content and low iron oxides. 4. Samples with calcite and serpentine. 5. Glass samples with crystalline phases.

Limestones and calcitic marbles give the same XRD results, then both consist of calcite, and therefore the above classification is not adequate to characterize absolutely the tesserae samples.

The petrographic analysis, based on the microscopical study of thin sections, gave additional results, regarding the characterization and the origin of the samples, results which can not gives the XRD analysis.

There are limestones whose grain size of calcite varies between 2 and 50 microns. There are also coarse marble samples with grain size 250 – 500 microns and finer marbles with grain size 30 – 135 microns.

The most important result from the thin section study is that the location and the origin of the limestone samples were found, due to the calcite grain size and the presence of fossils. According to this, the origin of the limestone samples is the area of Kissamos, which consists of limestones of the “Tripolis” and “Pindos” geological zones.

In the glass samples, apart from glass, rare crystalline phases, in minor amount, were found consisting of Ca, Sb, Sn, Pb, Cu, Zn. To ensure the identification of the crystalline phases of the glass samples the XRF analysis was necessary, which verified the chemical presence of the above elements. The presence of those elements is responsible for the color and the opaqueness of the glass samples.

Conclusions

The application of microanalytical methods depends on the material which is analysed.

For the study of stone mosaic fragments, apart from XRD, thin sections study is necessary, to find the characteristics and the origin of the raw material.

For the study and the characterisation of color glass fragments, the XRF analysis in any case is necessary to identify their chemical composition.

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USING MICRO-XRF AND RAMAN SPECTROSCOPY FOR NON-INVASIVE ANALYSIS OF ARTWORKS: TECHNIQUES AND APPLICATIONS

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Introduction

Archaeologists, historians, conservators and restorers use analytical sciences to provide information on objects of important historical value and determine their provenance, the environment in which they were created and also the causes of potential degradation/corrosion. Analytical studies of art items are different from the analysis of many other objects because they are often unique and irreplaceable so the use of non-destructive techniques is a key requirement.

In recent years, a number of technological developments have favoured the improvement of spectroscopic systems which have become very efficient and flexible for a wide range of applications, including art.

Experimental

Among the methods offering elemental information, micro-XRF is a tool of choice to obtain spatially resolved composition of a large variety of materials without any sample preparation and possible atmospheric pressure analysis to avoid causing damage to them. With a resolution ranging from 1mm down to 10 microns, individual particles and features can be analysed and element distribution images can be generated.

In a similar manner, identification of the chemical nature of a large range of compounds (pigments, gemstones, whether organic or inorganic, etc) is possible using Raman spectroscopy. Because art items often require the use of different laser sources to avoid fluorescence interferences and cannot be easily transported, a new compact micro-Raman system, the XploRA, will be introduced. It combines high-mobility, multi-laser excitation and extreme ease-of-use.

In addition, an innovative imaging technique using 2D scanning mirrors for recording maps on large paintings without moving them will also be described.

Results

Exciting recent case studies will be presented using these two techniques. Among them, a micro- XRF study has revealed the cat missing in the Hiroshima's version of "Daubigny's Garden", a famous painting of Van Gogh (Fig 1). Cases of an ancient Nepalese manuscript and a fragment of Italian fresco analysed using XRF will also be described.

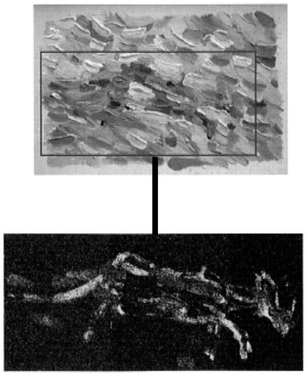
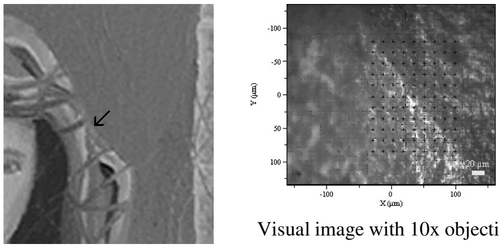


Figure 1: *micro-XRF enables to reveal the iron based pigment used to draw the cat in Van Gogh's painting*

The new Raman imaging technique has enabled to the determination of the different kind of pigments used in a very large painting. (fig.2)



Visual image with 10x objective

Figure 2: *Rutile, Calcite, Pigment Blue 15:3 and Ultramarine pigments has been found in this part of the painting*

Conclusion

New improvements in micro-XRF and Raman spectroscopy will be presented in application to non-destructive characterization of art objects.

O47

MULTITECHNIQUE CHARACTERIZATION OF LAPIS LAZULI FOR PROVENANCE STUDY BY MEANS OF IONOLUMINESCENCE

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Introduction

Lapis Lazuli is one of the oldest precious stone, being used as early as 7000 years ago: jewels, amulets and vases are examples of objects produced using this material. Only few sources exist in the world due to the low probability of geological conditions in which lapis lazuli can be formed.

Since art objects produced using this material are valuables, only non destructive investigations can be carried out to identify the provenance of the raw materials [1]. Ionoluminescence (IL) combined with PIXE/PIGE is a good candidate for this task. Similar to cathodoluminescence (CL), IL consists in the collection of luminescence spectra induced by MeV ion (usually protons) irradiation. Advantages of IL are the possibility to work in air on art works and the contemporaneous PIXE/PIGE analysis. The IL capability to distinguish Chilean Lapis Lazuli from Afghan has been demonstrated in a previous paper [2]. In the present work a systematic study was performed on Lapis Lazuli from different quarries using a multi-technique approach (SEM-CL, micro-Raman and SEM-EDS) to univocally identify and characterize luminescent phases. This characterisation was propaedeutic for IL/PIXE/PIGE measurements.

Experimental

Lapis Lazuli samples come from the Mineralogical Museum of Florence and were collected in four quarries: Sar-e-Sang Badakhshan (Afghanistan), Ovalle (Chile), Irkutsk near lake Baikal (Siberia) and Pamir mountains (Tajikistan). Seventeen thin sections were prepared and characterized at Torino University by means of cold-cathode CL (CL8200 Mk3), micro-Raman (Jobin Yvon, Mod. LABRAM HRVIS), SEM-EDS (Cambridge Stereoscan S360 and Oxford PentaFET EDS) and SEM-CL (Oxford MonoCL).

IL/PIXE/PIGE measurements were carried out at the INFN-LABEC external ion microbeam facility [2].

Results

Luminescence phases were classified by means of cold-cathode CL images and identified by means of micro-raman and SEM-EDS. SEM-CL spectra were collected in points of interest. In figure is shown an example of grey scale CL image from Chilean lapis lazuli (black is pyrite, bright yellow is wollastonite, deep blue is lazurite and so on); spectra of different phases are also shown in comparison with the dominant Siberian spectrum. Similar spectra are obtained in air using IL apparatus.

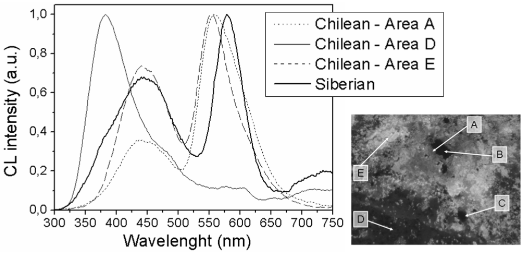

Figure 1: *CL image and spectra from Chilean lapis-lazuli: (A) orange, (B) black, (C) deep blue, (D) dark green, (E) bright yellow. The dominant spectrum from Siberian lapis lazuli is also shown.*

Conclusions

CL and IL spectra of different phases in lapis lazuli can be used to distinguish the provenance of this stone from the quarries studied. PIXE/PIGE analysis are helpful in cases in which IL spectra are similar or ambiguous.

Acknowledgements

This work was funded by Nuclear Physics Italian Institute, INFN (FARE and DANTE experiments).

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O48

THE USE OF A DIAMOND CELL FOR THE FTIR CHARACTERIZATION OF BINDING MEDIA AND PIGMENTS IN CONTEMPORARY PAINTINGS

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Introduction

The characterization of the binding media and pigments in contemporary pictorial artworks is important for designing safe conservation treatments, as well as for determining suitable environmental conditions for display, storage and transport. It is also essential to understand the ageing response of each of these new paint types to environmental factors, such as humidity, temperature, UV radiation and pollutants. What is more, chemical identification of a painting' s materials can also assist art historians in many ways, for example to identify the palette and the binding media, which an artist used most frequently, and to confirm or to dismiss suspicions about the authenticity of certain areas in a painting. Micro-FTIR spectroscopy in transmission mode, accompanied by a diamond anvil cell, can be effectively used for the identification of synthetic resin binders, pigments and extenders used in 20th century paintings [1].

Experimental

The samples studied are selected from modern paintings of The Macedonian Museum of Contemporary Art, which are in need of conservation. FTIR spectra were recorded with a Perkin Elmer Spectrum GXII spectrometer. This was equipped with an AutoIMAGE microscope and a MCT detector cooled with liquid nitrogen. Paint micro-samples were collected with a fine needle under a stereo-scope, were pressed in a cell fitted with diamond windows and placed directly on the analysis stage, under the focus of the microscope. Details on the experimental set-up are given in ref. [2]. The spectra were collected in transmittance mode in the range of 4000-700 cm^{-1} with a resolution of 4cm^{-1}, an aperture less than 100×100μm and 100 scans.

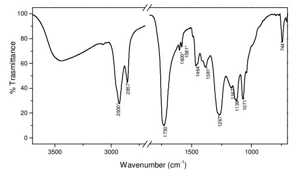
Results

A wide variety of modern materials were intentified. Both binding media such as oils, alkyd resins (Fig. 1a), poly vinyl acetates (Fig. 1c), cellulose nitrate, polyurethanes and extenders such as calcium carbonate, barium sulphate and calcium sulphate, gave a distinct spectrum. Numerous organic pigments were identified such as the azo pigments PY1, PY3 (Fig. 1b) and PR112; phthalocyanine green PG7 and blue PB15. Several inorganic pigments like chrome yellow and Prussian blue were also monitored. However, in some samples the strong and broad absorption of the extender or the medium did not allow the identification of the pigments, therefore the combined use of Raman spectroscopy was useful [3].

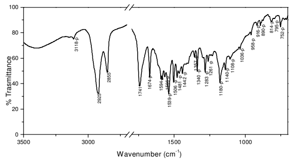
Conclusions

The diamond cell is a sampling method, which provides great improvement in the analysis of micro-samples. It is a non destructive technique with minimal sample preparation, enabling FTIR spectroscopy to rapidly and effectively differentiate 20th century paint material.

a) Pentaerythritol /linseed oil alkyd resin



b) Binding medium (oil) and azo yellow pigment PY3



c) PVA/VeoVa and calcium carbonate

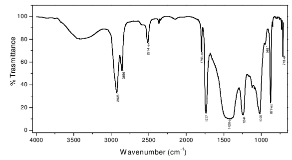


Figure 1: FTIR spectra of different samples from three different contemporary paintings from The Macedonia Museum of Contemporary Art.

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NON DESTRUCTIVE IDENTIFICATION OF ART OBJECTS USING MULTISPECTRAL IMAGES AND SPECTRA COMBINED WITH ACOUSTIC MICROSCOPY

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Introduction

The proposed technique is based on the combination of two modalities; acoustic microscopy and diffuse reflectance spectroscopy and imaging from the ultraviolet up to the mid infrared area of the spectrum (UV/VIS/nIR/mIR) targeting to non destructive stratigraphy identification of art objects. Using acoustic microscopy, the number of layers on the stratigraphy can be obtained using the information derived by the a-scan and c-scan. Using UV/VIS/nIR/mIR diffuse reflectance spectroscopy, the identification of materials that exist in each paint-layer can be achieved. The final result is material mapping images for the upper layer and the existing under-layers.

Experimental

For each point of the artwork inside a specific Region-Of-Interest (ROI), the prototype device is able to scan and acquire diffuse reflectance spectra from 200nm up to 4500nm as well as echo graphs from the paint layers. From the same regions, images are acquired in the IR area of the spectrum from the 1000nm up to 5000nm (Fig.1).

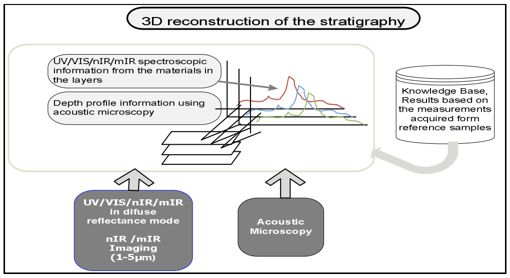


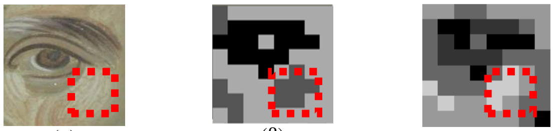
Figure 1: *The concept of the system.*

Results

The system was tested in a wall painting fragment in order to be evaluated. In Fig. 2 and in Fig. 3 the wall painting fragment and the corresponding infrared image from the 1500nm up to 5000nm is displayed respectively. In Fig. 4 (a) the ROI scanned with the spectrophotometer is displayed and in (b) and (c) the material mapping images which are created based on the acquired spectra in the UV/VIS and the IR spectral area respectively are also displayed. These mapping images are in agreement with the materials that exist in the painted object as well as the IR reflectance image displayed in Fig. 3. The region indicated with dashed line is also scanned with the acoustic microscope. In Fig. 6 (a), the a-scan acquired from the area of brush strokes with the acoustic microscope and the wavelet transform of it, revealing three echoes are displayed. The three echoes are generated by the successive interfaces that indeed exist in the stratigraphy.

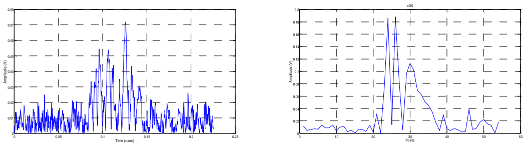
Figure 2*: Wall painting fragment.*

Figure 3*: IR reflectance image (from 1500nm up to 5000nm).*



(α) (β) (γ)

Figure 4: *Image of the ROI in the visible and the corresponding mapping images.*



(a) (b)

Figure 5: *The a-scan acquired from the area of brushstrokes (a) and the wavelet transform of it (b). The x axis is representing time and the y axis is representing voltage.*

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O50

PRINCIPAL COMPONENT ANALYSIS OF REFLECTANCE MEDIUM INFRARED SPECTRA FOR THE NON-INVASIVE IDENTIFICATION OF ORGANIC MATERIALS IN WALL PAINTINGS

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Introduction

The study, here presented, is part of a wide project (Organic Materials in Wall Paintings, OMWP) coordinated by the Getty Conservation Institute. The final objective of OMWP is to develop a protocol for the identification and mapping of organic binders in wall paintings, first testing the response of several techniques on model samples from the collection of the Tintori Center in Prato [1]. Recent advances in mid infrared fiber optic technology have made vibrational spectroscopy in reflectance mode very promising for the *in situ* non invasive study of painting [2]. The optical layout in use by the portable is 0°/0°, collecting both specular and diffuse reflection; thus spectral features depend not only from the infrared properties of the material but also on its surface roughness, making difficult their interpretation, An Principal Component Analysis (PCA) has been here tested in order to extract the relevant chemical information contained in the reflectance spectra, eventually covered by optical and matrix effects.

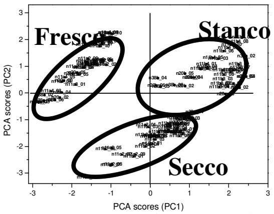
Experimental

Reflectance midFTIR spectra were recorded using the portable JASCO VIR 9500 spectrophotometer equipped with Remspec mid-infrared fiber optic probe. About 700 wall painting replicas of known composition (carbonate or silicate pigments mixed with casein, egg, oil) and painting technique (*fresco*, *stanco* and *secco*), have been employed.

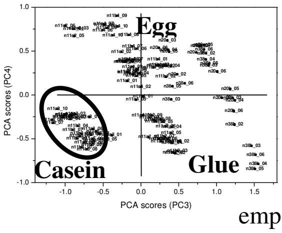
PCA, calculated by Golpe, has been applied to dataset constituted by midFTIR spectra as objects and frequencies in the range 900-4000cm^{-1} as variables.

Results

PCA has been carried out on resulting dataset containing the same pigment and three different binders (egg, casein and glue). The PC1-PC2 scores plot (~79% of the total variance) is reported in figure 1. It shows how the first two components are able to separate objects in to the diverse painting techniques (*fresco*, *stanco, secco*). The fresco cluster is remarkably separated by the *secco* and *stanco* groups. This behavior suggests that the FTIR in reflectance mode is largely sensible to the painting technique due to the strong influence of the carbonate matrix which stoutly distorts the spectral features, overall in the case of fresco where the binder is strictly bound with the carbonate plaster. The effect of the binder is evidenced by the third component PC3. In fact, casein are well separated along the third component as showed in figure 2.



The PC3 loading plot showed that the meaningful variables for the binder discrimination are those related the C-H stretchings that lie in a spectral region less affected by the carbonate matrix.



Conclusions

Wall painting replicas of known composition from the collection of the Tintori Center in Prato have been employed to test the multivariate approach for the treatment of reflectance mid-FTIR spectra. PCA, calculated by Golpe on pre-treated spectra, resulted to be very useful in managing spurious reflectance effects related to optical properties and matrix, highlighting the spectral features that are effective for discriminating different organic binders. These results represent the first step toward the development of an appropriate PCA modelling to be applied on spectra collected from real wall paintings.

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SECOND AND THIRD HARMONIC GENERATION MEASUREMENTS OF GLUES USED FOR LINING OF PAINTED ARTWORKS

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Introduction

An essential problem in art conservation is the re-lining of the reverse of a painted artwork. The original textile that supports the artwork with the age looses its elasticity, firmness and is no longer able to carry the picture layer. This fact raises the need to enforce the old textile by gluing a new one, a process called lining. The lining textile also deteriorates and needs to be replaced after a certain period of time. In this study we explore the feasibility of precise thickness detection and composition identification of different lining glues used in painted artworks by employing nonlinear measurements. The obtained information comprises a valuable tool for the assessment of the appropriate conservation treatment.

Experimental

A femtosecond laser has been used as excitation source at 1028 nm. The beam was directed to a modified optical microscope using suitable dichroic mirrors, and was focused tightly onto the sample by an objective lens with high numerical aperture [1]. The samples were placed to a round glass slide that fit into a motorized xyz translation stage. Third harmonic generation (THG) signals were collected and collimated in transmission mode by a condenser lens. After passing through a 340nm colored glass filter the signals were sent to a photomultiplier tube connected to a Lock-in Amplifier. Second harmonic generation (SHG) signals were collected in the backward direction using another photomultiplier tube connected to a Lock in Amplifier. A 514nm interference filter was placed at the photomultiplier input. Six different samples, representing the two main categories of the lining glues, were analyzed. The first category corresponds to natural materials of plant and animal origin (starch pastes, animal glues etc.). The second one corresponds to modern synthetic materials (acrylic resins, polyvinyl acetate etc.).

Results

Through THG measurements (Fig. 1) three different peaks can be distinguished indicating the interface between the different media. The first one corresponds to the air/glass interface; the second faint one to the glass/material and the third peak represents the material/air interface respectively. Consequently, the detected THG signals provide the proper information for the precise thickness determination of the lining glue layer. Complementary information related to the composition of the glues is obtained via the realization of SHG measurements (Fig 1). SHG signals are detected only from the collagen based glues since collagen, which has a highly crystalline not centro-symmetric triple-helix structure, produces SHG extremely effectively [2].

Conclusions

Non linear modalities comprise powerful, non destructive, diagnostic tools that provide detailed information regarding lining glues thicknesses and composition. The compact size of the employed excitation source and the reduced time of data acquisition (each measurement lasts less than a minute) make this innovative technique ideal for *in-situ* laser diagnosis of painted artworks.

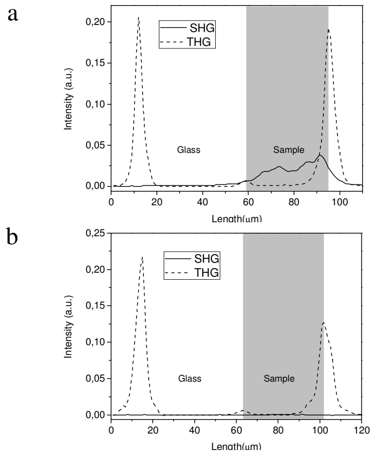

Figure 1: *Second and Third harmonic generation spot measurements from different lining glues a) from a starch paste where high SHG signals are collected due to collagen. The thickness of the paste is 35µm (based on THG measurements) b) from an acrylic resin where no SHG signals are detected. The thickness of the glue is 38 µm.*

Acknowledgements

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MICRO-FADING SPECTROMETRY: INVESTIGATING THE WAVELENGTH SPECIFICITY OF FADING

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Introduction

To determine the safety of display, and effectiveness of display policy in a gallery, a novel micro-fading spectrometer has been designed and constructed (1) (see figure 1) taking inspiration from the Whitmore design (2, 3). The optical instrument is capable of identifying light sensitive materials through direct fading of 0.25mm diameter sample areas. The microfading technique has typically been used to identify light sensitve pigments in artwork.

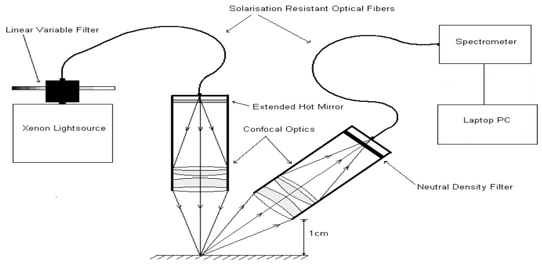

Figure 1. *A schematic representation of the Microfadometer design*

Experimental

Tate has applied the technique to analyze the behavior of pigments in anoxic conditions and also appraise the role of wavelength in the fading process.

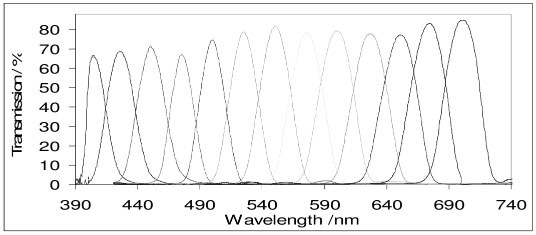

Figure 2. *The various filtered spectra used in fading experiments.*

In the later role by filtering the xenon lamp of the instrument by using linear variable filters it is possible to shape the fading spectrum. The filter bandwidth of this technique is 20 to 30nm FWHM (see figure 2). Via this technique the damage function of a variety of samples has been characterized.

An investigation of pigment and dosimeter damage functions for Prussian blue and Madder of the Turner Bequest (1850) took place. Prussian Green, Dragon's Blood, Litmus, Weld and dosimeters Blue Wools 1 and 2. LightCheck Sensitive, LightCheck Ultra. Rhodamine B and Litharge were also tested.

Results

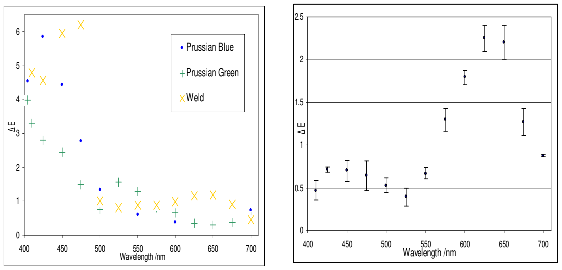

Figure 3. *(Left) Results from application to Lightcheck Sensitive 5 fold error bars +/- 1 standard deviation (Right) Results from application to Prussian Blue Prussian Green and Weld.*

Conclusions

Results of the new and more rapid way of defining the role of wavelength in fading compares well with previous data in the field. A good degree of reproducibility in the data was found (see figure 3).

A correlation between a material's reflectance spectra and its vulnerability to different regions of the visible spectrum has been demonstrated again. An exception was found in the case of Prussian blue which seems to exhibit a cut off wavelength above which fading ceases (see figure 3)

Acknowledgements

This research is funded by the Public Sector Research Exploitation Fund (PSRE) which sponsors the project at Tate.

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ANALYSIS OF VENETIAN-TYPE GLASS FROM LEZHA, ALBANIA

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Introduction

Numerous glass fragments were excavated from an occasionally discovered garbage site in an Albanian town of Lezha (ancient Lissos). Typologically, the fragments were classified as Venetian-type glass. Lezha was an important port under Venetian dominion and a merchant centre for salt and agricultural products. Grass objects could be traded as well. As no analysis of the contemporary glass from the area has been made up to now, the present results contribute to the understanding of the Venetian glassmaking and glass trade in the central Mediterranean.

Experimental

The analysis involved 40 samples chipped from the objects. The analytical methods applied were the combined PIXE-PIGE analysis [1, 2] and XRF. The ion-beam methods were performed at the Tandetron accelerator of the Jožef Stefan Institute, using proton beam in the air. Soft and hard X-rays were collected in separate spectra. Absorption of softest X-rays in the air prevented analysis of Na, Mg and Al, which were then determined according to their respective gamma rays induced by inelestic nuclear scattering. The glasses were also investigated by a source-excited XRF at the Centre of Applied Physics in Tirana; this metod provided better sensitivity for the elements around zirconium.

Results

Brief characterization by a hierarchical clustering method suggested that the glass form two distinct groups. One group was a typical Venetian or Venetian-like glass (façon de Venise); it was made of flux of halophytic plants as used for the Venetian white glass. Beside Venice, such glass was identified in several European glassworks of the 16th century [3].

The other glass group was made of flux of mixed sodium-potassium composition, but of the agents of greater purity. The concentrations of magnesium and aluminium oxides were bellow 1%, the contents of iron and titanium oxides were below 0.1%. Arsenic oxide was used for discoloration, which is an advanced feature in comparison with the Venetian glass that was discoloured by the addition of manganese oxide.

Conclusions

The analyzed glasses from Lezha distribute into two groups: one is Venetian or Venetian-type, while the other exhibits glass made of more refined raw material and decolourants. We suppose that this group represents glass that is younger, its production immediately following the façon de Venise phase.

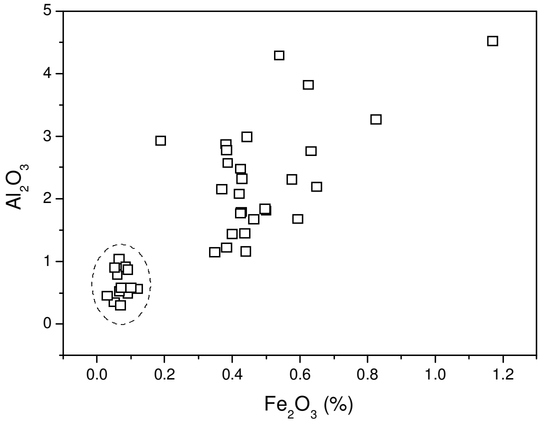

Figure 1: *Bivariate plot of the iron-aluminum oxide concentrations, showing two distinct groups.*

Acknowledgements

This work was part of the bilateral cooperation between Albania and Slovenia funded by the ministries of science in both countries. The authors are indebted to the archaeologist Dr. Gezim Hoxha for the glass samples given to our disposal.

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ELEMENTAL ANALYSIS OF ANCIENT GLASS BEADS BY MEANS OF COMBINED ION-BEAM AND SYNCHROTRON-BASED ANALYTICAL TOOLS

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Introduction

An integrated analytical approach, involving the synergy of laboratory and advanced X-ray microanalytical (EPMA, XRF, S-μXRF, 3D-XRF) and Ion-Beam Analysis (IBA) techniques, has been implemented towards the complete elemental characterization of a collection of archaeological glass products. The collection is composed from recently excavated beads (from graves located at the city of Thebes, Greece) that cover the period from Archaic up to the Hellenistic era (6th- 4th cent. BC) and glass vessel fragments ascribed to the Classical period (5th cent BC).

The aim of this work is to address technological features of this type of glass production and its evolution through different historical periods. Of particular importance is to provide a solid interpretation for their colouration associated with the presence of minor amounts of different metal ions, to clarify their mutual interaction, to understand elaboration of raw materials by means of high sensitivity trace element fingerprint and to reveal the manufacture technology of few selected layered glass beads. In addition, our analytical approach aims to evaluate different non-invasive analytical techniques in terms of their analytical range, sensitivity, accuracy and complementarity.

Experimental

Ion beam techniques have been applied on the recently established external ion beam set-up at the Tandem 5.5 MV accelerator of NCSR "Demokritos". The set-up utilizes, in an optimized geometrical arrangement, the simultaneous application of PIGE, RBS, low and high energy PIXE spectrometers with an additional mode of dose normalization by means of Si-K X-rays emanating by the 100 nm thin Si_3N_4 beam exit window. S-μXRF and 3D-μXRF measurements were carried out at the 7T-WLS/MySpot beamline of the BESSY II storage ring, Berlin, Germany utilizing an 19 *keV* excitation beam with ~20 *μm* spatial resolution. The FWHM of the confocal volume was measured to be ~26 *μm* at 8 *keV*. The analytical examination was complemented by microstructure compositional characterization (EPMA) and elemental analyses by means of a portable XRF (PXRF) spectrometer. All the measurements were performed on a representative collection of fifteen coloured glass fragments

Results

The external ion beam and PXRF analyses offered a consistent set of the major, minor and trace elements composition, whereas the later technique (PXRF) enabled a more accurate quantification of minor amounts of Sb_2O_3. EPMA provided complementary compositional information for major and minor elements, whereas in particular the sodium content was cross checked by means of EPMA, PIXE and PIGE techniques. These results clarified first queries regarding the manufacture technology (soda-lime glasses, average Na_2O 17.2 ± 2.7%) and identified the responsible colouring metal ions (Fig. 1). S-μXRF succeeded to probe at the very low μg/g region trace elements like Cr, Ni, Cu, Zn, As, Br, Rb, and Y, not identified by the rest of the techniques. The 3D-μXRF analysis of the so-called "eye" bead composed of three different colored layers offered in a non-invasive way unique information regarding its manufacture technology.

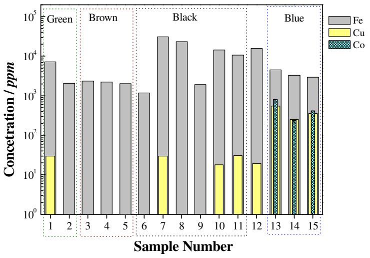

Figure 1. *Concentration of coloring metal ion by means of PIXE technique*

Conclusions

In the present study the utilization of advanced and laboratory analytical tools leaded to complete elemental characterization and enhanced understanding of the ancient glass technology.

Acknowledgements

Ivo Zizak at the 7T-WLS/MySpot beamline of the BESSY II and "DEMOEREUNA" project funded by NCSR "Demokritos" (2007-2008).

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O55

CROATIAN APOXIOMENOS – METAL COMPOSITION AND LEAD PROVENANCE STUDY

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Introduction

A bronze statue of the athlete with a strigil - the Apoxiomenos - was discovered at the seabed of the North Adriatic in 1999. The statue was complete, with the majority of the surface being covered with a layer of corrosion products and substantial quantities of organic limestone. These deposits protected the bronze from electro-chemical deterioration, although the back of the statue, which was buried in the sand, was to a large extent corroded. After the slow desalination process, the restoration and conservation process started in October 2000, as a joint project between Croatian Conservation Institute (HRZ), Zagreb and Opificio delle Pietre Dure (OPD), Florence. OPD has also performed comprehensive investigations of the statue by many physical and chemical methods [1]. The restoration process was completed in 2005 when the statue was exhibited for the first time.

Among the large number of analyses performed during restoration by OPD [1], probably the most important was ^{14}C AMS carbon dating of organic material (seeds) found inside of the statue. According to results of three samples, the sample age is between 100 B.C and 250 A.D. which proved the high historical value and importance of this statue. However, many questions about the origin of the statue, called now the Croatian Apoxiomenos, remained still to be resolved. Our more recent work on the analysis of bronze composition that is presented here will try to reveal part of the mystery of this exceptional ancient work of art.

Experimental

In the last 30 years lead isotope analysis has been successfully and frequently used for provenance studies of ancient metals excavated in the Mediterranean. [2} Using comparatively large database of ores and ancient metal artefacts from this region, the lead isotope analyses of bronze can identify the origin of lead, since in the Roman period the bronze (copper-tin alloy) used for casting large statues was alloyed with lead for technological reasons.

The elemental composition of the bronze of this statue was investigated by PIXE using 2 MeV proton beam in the RBI microprobe facility. The lead isotope analyses were done by MC-ICPMS at the Department of Earth Sciences of the University of Melbourne.

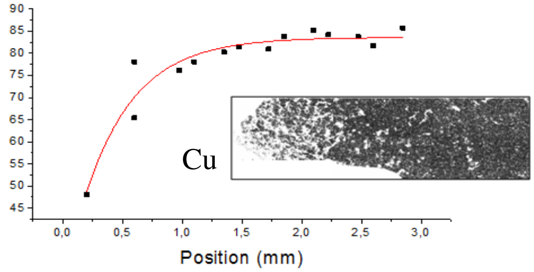

Figure 1. *PIXE analysis results for Cu in sample cross section. Left sample side was exposed to the seawater, with Cu being leached away.*

Results and conclusions

As it is seen from Figure 1, PIXE analysis showed electrochemical deterioration of bronze exposed to the seawater. Only the far right side of the sample could be used as a representative of the original bronze composition. The lowest levels of lead as measured for several samples were ranging between 1 and 4 %.

Lead isotope ratios were measured for 13 different samples, which showed identical isotope compositions, confirming that the statue was cast from one batch of bronze. The lead isotope composition of lead is consistent with some of the lead ores from the Sardinian ore deposits, however the possibility of the exploitation of the Balkan lead-silver deposits has to be also considered.

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THE HOARD OF BEÇIN: NON-DESTRUCTIVE ANALYSIS OF THE SILVER COINS

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Introduction

During excavations carried out at the medieval site of Beçin Kalesi in summer 2000 by a team of archaeologists from Izmir University in Turkey, a great number of coins could be found. It soon became clear that this archaeological find is one of the most important discoveries in Turkey.

The coins of main interest stem from the Ottoman Empire and were produced during the 16th and 17th centuries under the Sultans Murad III, Mehmed III and Ahmed I in 18 different mints. As most of the coins showed a green patina on their surfaces, it was agreed to take small samples of approximately 450 objects typical for the period as well as the mints.

The aim of the work was to determine their genuine fineness and to trace back to the ore deposits/mines supplying the metals used for manufacturing these objects.

Experimental

A broad combination of methods was applied in order to determine the main constituents, Ag and Cu, as well as the minor and trace elements characteristic for the provenance of the alloy used for the coins.

The samples were embedded in synthetic resin, cross-sectioned and analysed by micro X-ray fluorescence analysis (μ-XRF), scanning electron microscopy with energy dispersive X-ray microanalysis (SEM/EDX), proton induced X-ray emission spectroscopy (PIXE) and synchrotron micro X-ray fluorescence analysis (SR-XRF). For the μ-XRF measurements, the self-built instrument COPRA [1] could be used, equipped with a polycapillary for focusing the X-ray beam to a diameter of approximately 100-150 μm. The PIXE analyses were carried out at the accelerator AGLAE in the LC2RMF, whereas the SR-XRF measurements could be performed at the BAMline at BESSY II in Berlin.

Results

The Akce coins analyzed have a very high fineness. The average silver concentration found for the coins minted under the Sultan Murad III is 92.2%, for Mehmed III 92.5%, and for Ahmed I 91.4%. Therefore, no significant variations were found between the Ag content in the different reigns. However, a clear difference has been found in the Ag concentration of the different mints.

By comparing the trace element pattern a local assignment was explored. Even though no clear clustering was achieved, the coins of the different mints show distinct trends in their composition according to their origin.

Conclusions

Economic historians agree that from the 1580s until the 1640s the Ottoman Empire has gone through monetary instability arising from fiscal, economic and political difficulties, which led to the occurrence of frequent debasements. The silver content of the coins should have been reduced by 44% [2]. In contrast to these interpretations, the analyses have shown that the average silver content of the coins of all 3 Sultans is about 93%.

For the interpretation of the data a statistical analysis has been performed (principal component analysis). Significant clustering was obtained regarding the minor and trace elements composing the coin alloys.

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NON-DESTRUCTIVE DETERMINATION OF THE SILVER CONTENT IN ROMAN COINS DATED TO 308-311 A.D. BY COMBINED USE OF THE PIXE-ALPHA, XRF AND DPAA TECHNIQUES

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Introduction

In the last years a non-destructive protocol of analysis, based on the combined use of the portable PIXE-alpha [1] and XRF spectrometers and of the new DPAA (Deep Protons Activation Analysis) method [2], was developed at the INFN-CNR LANDIS laboratory for studying the Roman *folles* dated to 294–333 A.D. belonging to the Misurata treasure (Lybia), one of the most important finding of coins in the Mediterranean Area.

The main aim of the investigation was the determination of the silver content of the coins produced in different times and the study of the technique used to manufacture the *folles*.

It is well known that the Roman *folles* were produced with a few microns silvered patina and a bronze core containing a lower quantity of silver. Therefore the association of non-destructive surface and in-depth techniques is necessary in order to investigated in a non-destructive way the different layers of the coins.

The present paper discuss the results obtained from the analysis of 15 coins dated back to 308-311 A.D. produced by the mint of Carthago during the domination of the usurper L. Domitius Alexander. The analytical data obtained by the application of the above protocol of measurement allowed to make some considerations about the production of the *folles* in the Carthago area in this limited period of time.

Experimental

The association of different non-destructive techniques allowed to analyze different layers of the coins. The PIXE-alpha system [1], due to the definite range of alpha particles in the matter, limited the analysis to the patina of the coins while the DPAA method (Deep Protons Activation Analysis) was used to determine the silver content in their core, minimizing the surface effects due to the presence of the enriched patina [2]. More over the XRF measurements were also performed to explore the composition of the interface between the patina and the substratum of the coins. Due to the presence of the patina XRF data should be considered as qualitative.

Results

The data obtained from the analysis of 15 coins produced by the Carthago mint during the period 308-311 A.D. are shown in figure 1. The analysis evidenced that the silver content of the interior (DPAA data) is in many cases similar to the one observed in the patina of the folles (PIXE data). This result indicate a low skill of the mint to produce the Ag-enriched patina that usually characterize this typology of coins, probably due to a faulty application of the technique used by the others official mints for manufacturing this typology of coins.

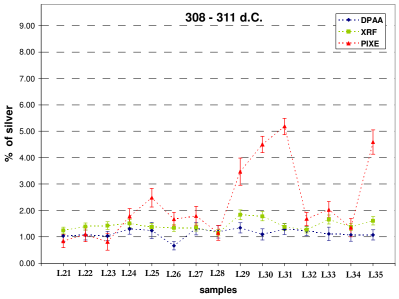

Figure 1: *The surface (PIXE) and interior (DPAA) analysis of silver contained in the 15 folles dated to 308-311 A.D. XRF results are also indicated.*

Conclusions

The association of different non-destructive techniques allowed to analyse different layers of the alloy composing the roman *folles* produced during the 308-311 A.D in the Carthago mint. A low content of silver was measured in the patina of the analysed coins allowing some historical considerations.

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μ-EDXRF AND XRD ON LEAD-BASED GLAZES

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Introduction

Chemical and mineralogical characterizations were performed on glazes applied to the ceramic body at different temperatures. The chemical investigation was carried out by micro X Ray Fluorescence (μ-EDXRF) and the mineralogical results with X Ray Diffraction (XRD) analyses. The main component found on this layer is SiO_2, the network forming agent. Because of the high melting point of SiO_2, several melting agents are needed, such as PbO, BaO, K_2O, MgO, Na_2O, FeO, ZnO, CuO, MnO, CoO and NiO. These materials decrease the temperature of the fusing process but it is necessary to have network stabilisers that increase the chemical and physical resistance of the glaze structure and decrease lead solubility. This is achieved with Al_2O_3 and sometimes ZrO_2 and CdO [1-2].

This investigation intends to be an initial output of the results we expect for lead-based glazes, since the complete study will be outstretched to real ancient faiences fragments from Coimbra (Portugal) from the XVI-XIX centuries [3].

Experimental

Three types of glaze (A, B, C) were applied, by submersion, onto the ceramic body and each one submitted to three different firing temperatures (800 ºC, 900 ºC and 1000 ºC). Glaze A: ancient glass (XVI century); Glaze B: ancient glass (XVII century); Glaze C: rustic glass.

The μ-EDXRF analyses were carried out with an OXFORD XTF 5011 Mo tube through a polycapillary lens, and the fluorescence radiation was collected with an SDD VORTEX-60X detector, thermoelectrically cooled. The spectrometer components are held in a vacuum chamber (10 mbar), allowing the radiation transmission through a Kapton window [4].

The XRD analysis were performed with a Philips X'Pert PW 3040/60 goniometer, using CuKα radiation, 30 mA and 50 kV, automatic divergent notch graphite monochromator and a step size of 1º/2θ/min in the 4-65º 2θ range, with data acquisition by Philips X'Perta Data Collector v1.2, after samples dried at 60 ºC, grounded and pulverized in an agate mortar. Identification of crystalline phases by XRD was carried out using the International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF).

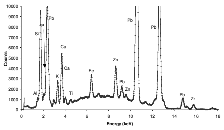
Results

The elemental results show that the SiO_2 and CaO are the major constituents followed by PbO in the case of Glaze A (fig.1). After submitting the three glazes to the three different temperatures, we can see that they remain with a mate aspect. This fact helps to corroborate the elemental profile exhibited, mainly out of aluminium-silicates. The firing temperatures of the glaze should not be greater than 1000ºC, in the case of a double firing, which we suspect that is the case of faiences from this region.

Conclusions

Analysing the elemental and compositional profile we can attribute manufacture techniques to the national ceramic production, namely because there are still misdated pieces in time and place. Coimbra production is often attributed to Lisbon production due to a lack of scientific data, which we aim to overcome.

μ-EDXRF spectrum of glaze A.



Firing temperature elemental dependence on glaze A.

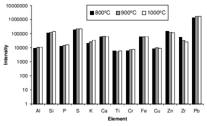


Figure 1: *Elementall results on the glaze A.*

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IMPORTANT CONSIDERATIONS IN APPLYING X-RAY MICROANALYSIS TECHNIQUES FOR DAMAGE ASSESSMENT OF OUTDOOR COPPER BASED MONUMENTS

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Introduction

The paper discusses the diagnostic analysis using XRF and XRD carried out for the famous outdoor copper based monuments, Theseus and Kolokotronis in Athens, and Kolokotronis in Nauplion. It discusses the best systematic approach to apply such techniques for damage assessment of monuments. It highlights important considerations and the benefits of non-invasive in-situ analysis, but also the limitations, and the important information that can be obtained through destructive analysis. One main consideration is the identification of representative locations for measurements and samples. Such plans require systematic documentation of nature and properties of the material at these locations, and the type of environmental exposure.

Experimental

During the monuments' survey, visual examination, historical research, and estimation of the impact of specific climatic conditions was necessary prior to the design of a sampling/measuring plan. These locations once selected were photographed and described in detail.

The equipment used for XRD analyses of all the three monuments, is described elsewhere [1]. The quantitative analysis was carried out by the Rietveld Method, using the software TOPAS from Brucker company. The sum of the crystalline phases was normalized to 100%. At Kolokotronis in Athens, an adequate sample size could not be collected for XRD quantitative analysis due to the type of environmental exposure. Principal Components Analysis on the presence and quantity of different corrosion products to the exposure conditions of the sample location was carried out for the located at Nauplion Kolokotronis monument [1]. For Theseus monument, in particular, a destructive analysis using metallographic cross section of a small piece of metal provided invaluable information concerning the unique electrotype technology applied by the German WMF company.

In 2001, a portable radioactive based XRF instrumentation was used to analyze the surface and composition of the Kolokotronis monument in Athens [2]. In 2005, an improved XRF equipment based on a low-power laser activated X-ray source was assembled and utilized on the Kolokotronis in Nauplion. With the newly developed XRF spectrometer major amounts of sulphur or/and chlorine present on the monuments surface could be detected. However, the particular weather and field conditions (high temperature, direct exposure to sunlight) hampered its successful implementation during the one day on-site analysis at Nauplion. Further improvement in the design and integration resulted finally to a handheld type of XRF spectrometer (described in detail elsewhere [3]). This later version was utilized at Theseus in Athens.

Results

The in-situ XRF analysis at Kolokotronis in Athens provided quantitative information regarding the bulk composition (at pre-cleaned spots) and the variation of the Zn/Cu and Sn/Cu weight ratios at eighteen (18) pre-selected patina spots. The XRD results showed that all three monuments had chloride-containing corrosion products, but with more occurrences for the monument in Nauplion closer to the sea than the others. The Theseus monument made of copper had high amounts of oxides such as cuprite on the surface, which can be related to the manufacturing process. .

Conclusions

XRF and XRD are important investigative tools for the assessment of damages to outdoor copper based monuments. However, the case studies prove how to apply the technique is specific to the type, condition and environment of the monument.

Acknowledgements

Funding by EC program Culture 2000 and Archimedes-Education and Initial Vocational Training Program are gratefully acknowledged.

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EDXF IMAGING OF PB DEPTH PENETRATION IN GLAZED CERAMICS USING A MICROPATTERN GAS DETECTOR

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Introduction

A simple system for energy resolved x-ray fluorescence imaging using a room temperature, 2-D sensitive Microhole and Strip Plate (MHSP) filled with pure xenon [1] is used to study lead distribution with the depth in ancient pottery. The detector has an active area of 28x28mm^2, an position resolution about σ=125μm, an energy resolution (R_E) of about 825eV (FWHM)@5.9keV and a rate capability up to 0.5MHz. Commonly used XRFI systems are based either: in scanning, like SEM with Energy Dispersive Spectrometers (EDS), or microfocus X-ray with spectrometers[2]; or in full field of view systems based on CCDs or on the medipix[3,4].

Recent developments on MicroPattern Gas Detectors (MPGD), have shown excellent properties for single photon counting imaging and good for EDXRF [5,6,7] applications. The physical operation of MPGDs does not allow the R_E present in other systems, but allow fair R_E among a good number of features, namely: absence of background (by setting a threshold); <1keV detection capability; possibility of large detection areas (>10×10cm2) and; low cost.

Experimental

The XRFI system consist of an x-ray excitation tube, a 200 μm tungsten pin-hole and the 2D-MHSP based detector placed like shown in Figure 1.

Once the detector system is able to record position and energy information, a map of the elemental distribution in the sample can be obtained by selecting their x-ray characteristic photons.

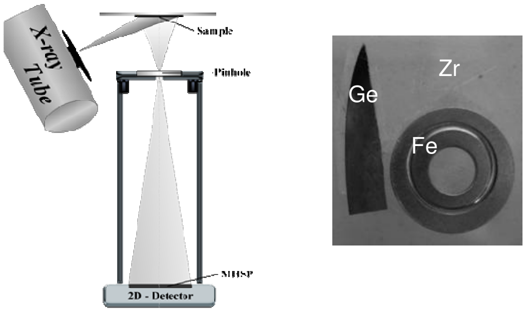
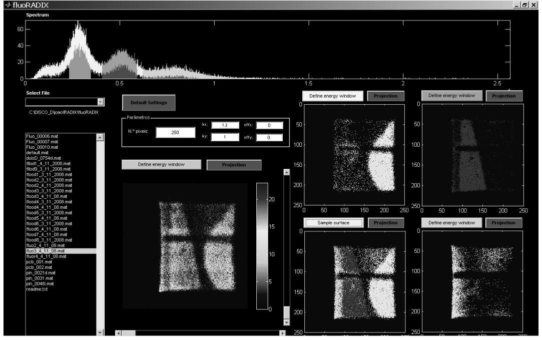


Figure 1: *XRF imaging system and sample.*

Results

The dedicated software allow us to chose the energy regions of interest (ROI) and plot the respective image only with photons with energy within the ROI, e.g. Figure 2.



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offy: 0

Figure 2: *Total pulse height spectrum together with the raw x-ray fluorescence image (left), the individual elemental images and the resulting image combining the three selected elements (bottom left), from the sample photo, Fig.1, are presented.*

Conclusions

The excellent single photon counting capability of the system combined with the good position resolution, R_E and rate capability up to 0.5 MHz, allows an efficient elemental and position detection of fluorescence x-rays from multi-elemental samples.

Acknowledgements

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INDONESIAN PAINTING: PIGMENT CHARACTERISATION OF MODERN BALINESE PAINTING BY RAMAN MICROSCOPY

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Introduction

The colour palette from three 20th century and one 21th century Indonesian paintings from the island of Bali was determined by Raman microscopy. Those paintings are typical of Hindu religious iconography, mainly with themes, episodes and battles from the literary epics [1]. There is very little information concerning the artistic techniques from this region of the world. Another interesting aspect of such a study would be to observe if within the time span of one century there was a change in the palette. In order to add more insight into modern Indonesian painting techniques the findings were also compared with samples of representative pigments commonly used by Bali artists, donated by a Balinese painter.

Experimental

List of paintings: AZ.760 dated from the first decades of the 20th century, 8.1ID12 dated from 1950, 8.1ID4 dated from 1970, and 8.1ID23 dated from 2003. Samples were removed from each painting, and were chosen to represent the colour palette. The pigments were analysed as given. The main analytical techniques used were: Raman Microscopy (Jobin Yvon, LabRam 300, laser He-Ne 633 nm and solid state 532 nm) for pigment identification, FTIR (Nicolet Nexus spectrophotometer with a Continuum microscope) for binding medium identification, and micro X-ray fluorescence spectroscopy (μ-XRF, Intax GmbH, Mo anode) for elemental identification.

Results

The most striking finding of our study was the increasing substitution of natural pigments by modern synthetic ones. On the other hand our task of identifying those modern organic synthetic pigments was the biggest challenge, since there are many chemical classes and hundreds of different pigments catalogued [2]. Although the pigments donated were mainly inorganic ones (red and yellow ochre, bone white, carbon based black and vermilion) the green and yellow pigments are most likely lakes. μ-XRF showed the presence of Ca and Fe usually indicative of metal salts. In all paintings the white is identified as starch, a common binder usually got from rice, used for priming the canvas in Indonesian painting [3]. The red pigments were substituted from the common red ochre and vermilion (in AZ.760 and 8.1ID12) to β-naphtol red pigments lakes. Similarly the yellow pigments move from yellow ochre to a resin pigment and a diarylide pigment. The blue and green colours showed interesting features since they are composed of mixtures. Ultramarine, the synthetic lazurite was always used, but in, 8.1ID4 and 8.1ID23 it is mixed with a blue phthalocyanine and anatase, a titanium oxide (Fig. 1). This feature indicates the need of exploring different hues for the same colour. The green colour was obtained with the same mixture, but probably a green phthalocyanine was employed. More traditionally the black colour was a carbon-based pigment, and in some paintings there is evidence of a bone black, with the phosphate Raman band at ca. 960 cm^{-1}.

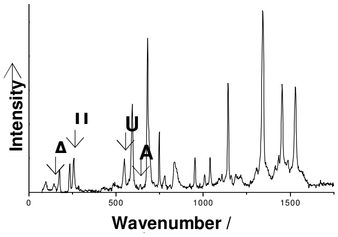

Figure 1: Raman spectrum of the blue colour in painting 8.1ID4, showing the main Raman bands of ultramarine blue (U), anatase (A) and a blue phthalocyanine.

Conclusions

Raman Microscopy proved to be a powerful tool to characterise the colour palette of contemporary Bali painting. The pigments used range from natural inorganic pigments to modern organic (synthetic) ones. The main classes of those pigments and in cerrtain cases the particular pigment were identified.

Acknowledgements

V. S. Muralha would like to acknowledge Fundação para a Ciência e Tecnologia (FCT/MCTES) for a post-doctoral grant (SFRH/BPD/42286/2007). The authors would like to thank the Museu do Oriente and Museu Nacional de Etnologia for allowing the access to the paintings and the painter I Gusti Wedagama for sending the pigments.

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USE OF X-RAY-BASED MICROANALYTICAL METHODS FOR EXPLANATION OF ORIGIN AND CORROSION OF COPPER-BASED PIGMENTS

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Introduction

The correct identification of pigments and all accompanying phases found in colour layers of historical paintings is relevant for searching their origin, route of pigment preparation and use, and for specifying their further degradation processes. Such a detailed description is essential for regional provenance classification of anonymous artworks.

We applied successfully the analytical route combining non-destructive in-situ X-ray fluorescence measurements with subsequent laboratory investigation of microsamples by X-ray-based methods to get efficiently all the data relevant for mineralogical and geological interpretations of the pigments origin. Within this mineralogical approach we have described, for example, the regional provenance of iron reds used in some Slovak Gothic panel paintings and this feature was then used as a criterion classifying different paintings to the same mediaeval workshop [1].

The aim of here presented work is to find certain traits allowing to distinguish between natural and synthetic Cu-based salts (carbonates, chlorides, sulfates etc.) used as pigments and to explain their chemical degradation resulted in the change of their original colour. The results are based on measurements of selected paintings by microanalytical tools and on the data obtained from model corrosion experiments with reference materials.

Experimental

The microsamples were examined by optical microscopy (Olympus BX60), SEM-EDX (Philips XL30CP) and powder X-ray microdiffraction - micro-pXRD (PANalytical X'Pert PRO diffractometer equipped with a 0.1 mm monocapillary). Details on the experimental set-up are given in ref. [2]. We found the laboratory micro-pXRD as an effective routine method for direct phase analysis of small samples containing crystal constituents with no need of their pre-treatment.

Results

Azurite, malachite, atacamite, paratacamite, brochantite, posnjakite and other Cu-containing phases were identified in fragments of painting layers (Fig. 1). The natural origin of azurite and malachite was indicated by presence of accompanying Cu-Zn arsenates which allows prediction of their provenance. The synthetic malachite was identified according to its typical spherulitic crystals. The corrosion of blue azurite to green basic Cu-chloride was clearly evidenced on some wall paintings and polychrome sandstone sculpture exposed to action of salts and moisture – in a good agreement with the results of laboratory experiments.

Conclusions

The distinguishing of different Cu-based phases allowed describing the alteration processes and colour changes of original paints. It was also possible to undoubtedly identify admixtures indicating natural origin of e.g. malachite. It is important, because malachite can also be present as the most stable product of alterations.

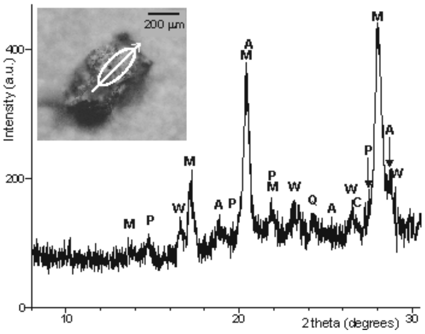

Figure 1: *XRD pattern of the fragment of the 14th century wall painting from Sazava Monastery, Czech Republic; the ellipse and the arrow remark the analysed area and the direction of the incident beam; M-malachite, A-atacamite, P-posnjakite, C-calcite, Q-quartz, W-weddelite.*

Acknowledgements

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ABSTRACTS

POSTERS

THE ITALIAN PAINTING OF THE 17TH CENTURY CONTRIBUTIONS OF A NON-DESTRUCTIVE INVESTIGATION

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Introduction

The aims of the present work are to study the colour palette and the painting technique used by an Italian painter, Valerio Castello. He was active in the first half of 17th century (1624 - 1659) in Genoa (Italy). Inorganic pigments were recognized by means of X-ray fluorescence, reflectance spectrophotometry and UV methodologies. These measurements allowed us to identify the colours palette used by this artist. Five paintings have been selected, characterized by different grounds and supports (canvas, wooden panel, copper and slate) and any sample of painting was not taken. From ten to twenty measurements to characterize the different pigments for each artwork have been made. The results allowed us to identify the palette of this author, which includes white and red lead, cinnabar, natural ultramarine blue, Co smalt, malachite, maybe copper resinate, and carbon black, gold both in leaf and powder, different kinds of natural earth. Could be used red lacquer as well.

Experimental

The methodologies employed were different and complementary: X-ray fluorescence spectrometry, which allows to recognize the elemental composition of the inorganic materials and spectrophotometry in the visible region, that gives an exact measure of the investigated colour.

X-ray fluorescence spectrometry

Elemental analysis on pigments was carried out by means of a portable equipment *Lithos 3000* from *Assing*. The apparatus consists of a molybdenum tube equipped with a zirconium filter and a semiconductor Si (Li), Peltier cooled, detector. Spectra were recorded with a measure time from 120 to 300 s, the current tube was 300 mA and the voltage was 25 kV. Specific software was used to elaborate the experimental data.

Reflectance Spectrophotometry in the visible region

A *Minolta CM-2600* portable spectrophotometer equipped with a Xenon lamp (D65 standard illuminant) and an integrative sphere was used to perform the colour measurements. The light, pulsate on painted surface in correspondence of the selected spots, is reflected by the sample with an angle of 8°. It is captured by a Si-Li photodiode that allows us to obtain the overall spectrum, between 400 and 700 nm with an interval of 10 nm, characteristic of the investigated point. The colour coordinates are based on CIEL*a*b* system. L* indicates lightness while a* and b* are the coordinates of chromaticity, based on the theory of the opposite colours: the coordinate +a* and -a* indicate red and green values while +b* and –b* indicate respectively the yellow and blue values.

UV fluorescence

These measurements were carried out using both a commercial UV lamp with a digital photographic apparatus and a digital microscope, *Dino-lite*, equipped with visible and UV light, at magnifications of 50-100 x.

Results and Conclusions

The experimental data obtained according to the above described methodology, yielded the following considerations:

1. The majority of the inorganic pigments used to obtain his paintings, when the painter worked with different supports, could be identified by coupling the data coming from X-ray fluorescence, UV fluorescence and from reflection spectra [1,2];
2. As the form of the reflectance spectra remains unchanged in many cases, while L* varies, we could observe that the same pigment was used in a mixture both of white pigment (lead white) or black carbon. This effect allows the artist to obtain the highlights and outlines;
3. The complementarity of colour combinations was also observed in Valerio Castello' paintings;
4. The results for the different works, if grouped on the basis of the different colours, allow us to obtain the palette used by this painter;
5. As it regards the kind of preparation layers of the different artworks, their composition was ascertained by checking and comparing the proportions of some characteristic elements as calcium, strontium, sulphur and lead which resulted similar.

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SEC/MALLS TECHNIQUE IN PAPER DEGRADATION STUDIES

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Introduction

Size exclusion chromatography (SEC) has proved to be an excellent tool for the analyses of paper materials of historical or artistic value. Combined with Multi Angle Laser Light Scattering (MALLS) detector it provides comprehensive information on both direct values and distribution of the molecular mass of cellulose samples, which is of great importance in the studies of paper degradation kinetics. This micro destructive technique seems extremely useful not only to assess current condition of papers but also to estimate their life expectancy and durability.

The routine application of SEC/MALLS for the analyses of archival papers requires several important technical problems to solve. The most crucial of them include preparation cellulose samples and determining the specific refractive index increment for their derivatives. Also, since viscometry is the most commonly used for the determination of degree of polymerisation (DP) of cellulose in the laboratories dealing with modern and archival samples the question arises whether the results obtained with both methods coincide and to which extent they can be used interchangeably. The correlation results may shed some light on the meaning of the viscometric DP values.

The paper intends to demonstrate some technical aspects connected with the calibration of SEC/MALLS system and the correlation with viscometric results. This will be presented in the broader context of our research of paper degradation mechanisms.

Experimental

Using SEC/UV (Breeze, Waters) and MALLS (Dawn Heleos, Wyatt) and classical viscometry, the different types of aged model paper (TNO, The Netherlands) were examined. SEC was done for cellulose tricarbanilate (CTC) in tetrahydrofurane. CTC samples were prepared in the way described elsewhere [1]. Viscosity measurements were done with capillary viscometer in 0,5M cupriethylene diamine (CED) solution according to standard [2]. Paper samples were aged in artificially polluted environment (NO_2, SO_2 or both) at room and at elevated temperatures.

Results

For the sake of the results correlation the molecular masses of CTC were re-calculated into the degree of polymerization (DP) of cellulose assuming the total substitution of cellulose and compared with average DP values obtained from viscometric measurements.

The example of correlation plot obtained for model paper made of pure cellulose is presented in Figure 1. From the plot, the Mark-Houwink coefficients were calculated and compared to the literature values.

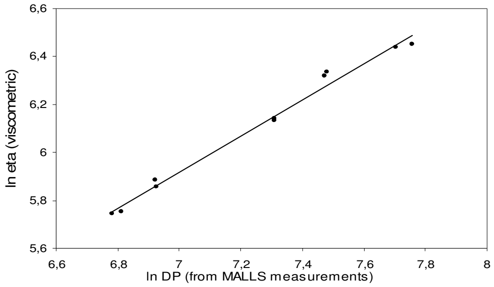

Figure 1: *Correlation between viscosity and degree of polymerization from SEC/MALLS analysis.*

Conclusions

1) The increments of refractive index were found for several paper types. This allowed using direct values of molecular masses for the kinetic studies of paper degradation.
2) The results show excellent correlation between DP values of cellulose obtained from traditional viscometric method and SEC analyses with light scattering detection for several tested types of paper.
3) The viscometric technique could be regarded as the primary method of molecular weight determination for polymers (meaning: requiring no standards) only when Mark-Houwink coefficients are known for a given system (sample/solvent/temperature). The SEC/MALLS results provide new data for recalculating these values.

Acknowledgements

Financial support from EU (6th Framework Programme, contract No. SSPI-006584–*PaperTreat* Project) and Polish Ministry of Science and Higher Education (grant SPUB 3084) are greatly acknowledged.

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ASSESSING EARLY PHOTOSYNTHETIC GROWTH ON MONUMENTS BY *IN VIVO* CHLOROPHYLL FLUORESCENCE

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Introduction

The biomass of cyanobacterial and algal communities dwelling on stone monuments can be quantified through the chlorophyll *a* estimation using chlorophyll extraction procedures. This technique is one of the best methods for the quantification of photosynthetic biomass in aquatic and terrestrial ecosystems. However, one of the disadvantages inherent to this method is the scaffolding and sampling procedure required, which takes more relevance when samples are collected from cultural heritage assets. In recent years, the measurements of *in vivo* chlorophyll fluorescence were introduced in the analysis of stone cultural heritage as a reliable and non-destructive technique for chlorophyll *a* estimation. This method has been used to detect photosynthetic microorganisms on monuments, monitor preventive treatments and to characterise different stone types [1]. It consists of a spectrofluorometric method employing a fibre-optic accessory, which allows measurements of *in vivo* chlorophyll *a* fluorescence on solid substrates without sampling procedures. The present work aims to assess the efficacy of these two methods of estimating photosynthetic biomass on stone.

Experimental

Different limestone probes from Mediterranean Basin lithotypes were inoculated with cyanobacteria and microalgae and incubated during three months under laboratory conditions. During different incubation times, stone probes were analysed using the chlorophyll extraction technique as described by [2]. For *in vivo* chlorophyll *a* fluorescence analysis, emission spectra were determined using a spectrofluorometer (Fluorolog-3 FL3-22) fitted with a fibre-optic platform (Horiba Jobin Yvon F-3000). The measurements were carried out on the inoculated surface of each stone probe at an excitation wavelength of 430 nm and using slits of 4.5 nm.

Results

Photosynthetic biomass estimated by the chlorophyll extraction technique revealed a great increase of photosynthetic biomass over three-month incubation for the limestone probes presenting high porosity (average value 2.40 ± 0.75 μg cm^{-2}). Regarding the *in vivo* chlorophyll *a* fluorescence measured on the surface materials, the emission spectra showed the typical chlorophyll *a* fluorescence peak at 684 nm (Fig. 1). During three months, high fluorescence intensities were obtained for the lithotypes presenting green biofilms covering the stone surfaces, corresponding to the lithotypes of low porosity. In contrast, for high porosity lithotypes, the chlorophyll *a* decreased over the incubation time.

Conclusions

The amount of chlorophyll *a* estimated by the extraction technique allowed quantifying the complete amount of photosynhetic biomass growing in the stone probes, whereas the *in vivo* chlorophyll *a* fluorescence only estimated photosynthetic biomass developing on the stone surfaces. However, the results obtained from both techniques permitted to corroborate that endolithic growth occurred for high porous stones. Moreover, the spectrofluorometric method showed high sensitivity for the detection of very low concentrations of chlorophyll *a* allowing the detection of photosynthetic microorganisms at an early growth stage on the stone surfaces. Our results revealed that both techniques are complementary.

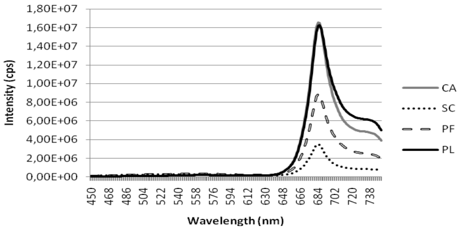

Figure 1: *Chlorophyll fluorescence spectra for each lithotype after three months of incubation.*

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P4

CHARACTERIZATION OF DAMAGES INDUCED BY LIBS ANALYSIS ON ARCHAEOLOGICAL OBJECTS USING OPTICAL PROFILOMETRY

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Introduction

Laser-induced breakdown spectroscopy (LIBS) technique is an attractive and powerful tool for the analysis of archaeological and art objects as it is demonstrated in the literature [1]. However its invasiveness, although low, limits its applicability and can be a cause of rejection of restorers and conservators for their analyses. The principle of LIBS technique is based on the detection of the light emitted from the ablated species of a material when an intense laser radiation is focused on its surface. Hence, the elemental composition of solids can be obtained in a fast way and without sampling. In any case, this spectroscopic analysis requires a removal of a small amount of material and, therefore, a little damage or alteration is generated on the irradiated area. On the other hand, in recent years, a different approach has been introduced in the LIBS measurements with the use of double pulse irradiation in order to improve the analytical performance of the technique [2]. This approach could be interesting for the cultural heritage analyses in the sense that a lower material removal can be obtained depending on the experimental arrangement used.

The goal of this work is to quantify the damages or alterations produced when LIBS measurements are achieved on archaeological specimens, using the optical profilometry technique. The study focuses on the conventional irradiation scheme, e.g. single pulse configuration, but also on the double pulse approach in orthogonal geometry.

Experimental

Specimens of different nature (paints, ceramics and metals) have been selected for the LIBS measurements in order to determine the damages generated in each case.

The LIBS experimental set up for the single mode configuration consisted of a Q-switched frequency-doubled Nd:YAG laser emitting at 532 nm in 6 ns pulse duration. The double pulse configuration was carried out with the reheating scheme (orthogonal geometry), where the characteristics of the second laser were similar to the first one. The plasma light was collected through a fiber optic onto the entrance of an echelle spectrograph coupled to an ICCD camera.

Finally, the irradiated areas resulting from the LIBS measurements were characterized with the aid of an optical imaging profiler which combines confocal and interferometry techniques.

Results

For each specimen, the LIBS signal has been compared in both configurations: single and double pulse modes. Figure 1 shows the enhancement with double pulse compared to single pulse which is noticeable in the spectrum, not only in intensity but also in spectral resolution and signal-to-noise ratio.

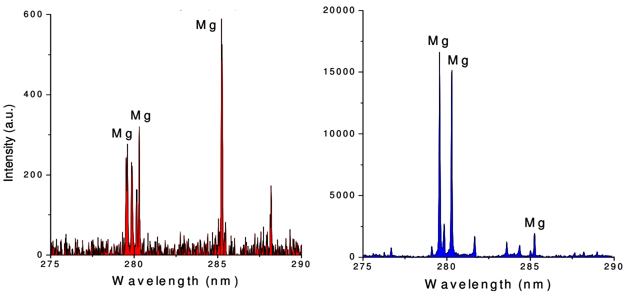

Figure 1: *LIBS spectra obtained with single pulse (left) and double pulse (right) configuration*

The spectroscopic data have been complemented with surface topography measurements (ablated volume, 3D imaging (Fig. 2), roughness), in order to evaluate if the LIBS induced damages are acceptable and if the double pulse configuration brings a real enhancement in terms of material removal rate.

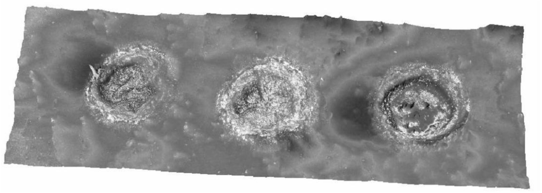

Figure 2: *Surface topography of craters generated by LIBS analysis, using confocal profiling mode*

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P5

A NEW SPECTRAL IMAGING APPROACH FOR THE IN-SITU ASSESSMENT OF THE CLEANING INTERVENTION ON STONEWORK

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Introduction

An important issue in every cleaning intervention on Cultural Heritage objects and monuments is the monitoring and follow-up of the cleaning process. Any unnecessary or excessive actions may alter irreversibly the original surface and thus attention should be paid to ensure that no damage could occur to the object during cleaning. Towards this aim multi spectral imaging techniques were considered and a new approach was investigated aiming to follow on-line the removal procedure and evaluate non-destructively the cleaning level.

Experimental

The suggested methodology is based on the optical properties of light penetration in matter. A custom made portable spectral imaging system (IRIS) was used to acquire images, obtained at various spectral bands, with a bandwidth of 25nm FWHM, during the cleaning intervention. The images were then processed in order to calculate their differences and get a visual estimation of the cleaning depth.

Results

This novel approach was tested in the laboratory during laser cleaning trials on polluted stonework enabling the detection of thin crust layers remaining on the under-cleaned marble surfaces. It was shown that maximum contrast was achieved when the 950nm and 450nm spectral images were divided. This is due to the fact that light at higher wavelengths (950nm) penetrates into the crust; being reflected from deeper layers, while at shorter wavelengths (450nm) light interacts mostly with the surface. A graphical representation of this reflectance ratio is given in Figure 1, showing the thinning of the crust layer (from about the 3rd up to the 6th pulse) while further cleaning (more laser pulses) does not change the reflectance ratio implying that the optimum cleaning level has been exceeded and damage may potentially occur.

Following this methodology the spectral images of certain snapshots of the cleaning intervention were processed to get an intensity ratio map which enables real time monitoring of the cleaning level. As shown in Figure 2 the under-cleaned area (1) does not appear in our processed image (image 2b), while the optimum cleaned (2) and the over-cleaned (3) areas show remarkable reflectance differences enabling the determination of a safe cleaning threshold.

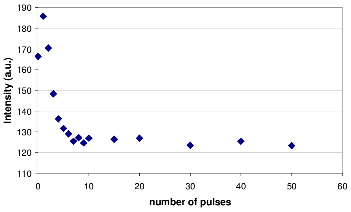

Figure 1: *Intensity graph of the reflectance ratio (950nm-450nm) recorded upon irradiation (1046nm, F=0.5 J/cm^2) of a marble surface with pollution crust over successive laser pulses. The observed peak (at 2 pulses) denotes optimum cleaning while the plateau after the 10th pulse indicates substrate damage.*

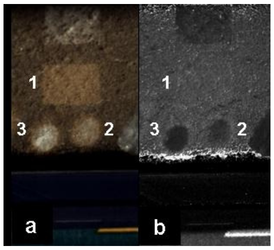

Figure 2: *Visible (a) and intensity ratio (b) images of a polluted marble surface showing cleaning tests at various stages: 1) undercleaned, 2) optimum and 3) damaged.*

Conclusions

The methodology was tested successfully on a series of different cleaning cases of encrusted stonework and thus the principle of operation was proved. Obviously the applicability of this approach is not restricted to laser cleaned surfaces and may also apply for the monitoring of any cleaning technique (micro air-abrasive, etc). A detailed presentation of the results will be demonstrated while the potential of its wide application on everyday conservation practice on stonework will be discussed.

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P6

NON-DESTRUCTIVE DEPTH-PROFILING OF PHOTO-AGED DAMMAR VARNISH USING SPECTROSCOPIC ELLIPSOMETRY

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Introduction

The depth profile of photodegradation chemical alterations in picture varnishes has been recorded using LIBS, DTMS, SEC, MALDI-TOF-MS and ATR-FTIR [1]. Data on the depth-wise optical properties of the films is rare and the only technique used is UV/VIS spectrophotometry [1]. However, the reported procedure introduces inevitable errors to the final profile due to the interaction of the laser beam with the natural polymer and lack of precise depth measurement. Towards this direction, this work aims to apply the technique of Variable Angle Spectroscopic Ellipsometry (VASE) on artificially UV aged dammar varnish layers and fit the results according to a multi-layer model. We have to note here that spectroscopic ellipsometry has already proved useful in the optical characterisation of fresh and aged picture varnishes [2].

Experimental

Details on sample preparation and ellipsometric equipment are given elsewhere [2]. The ellipsometric calculations are based in the measurement of the ratio of the reflected intensities of two mutually-perpendicularly polarised light beams. A model is constructed, based on the assumed values of the unknown physical parameters. The actual value of these parameters are determined through the use of an iterative regression fitting computer algorithm which minimizes the error between the measured data and the model-generated data by adjusting the physical parameters of the model [3].

In our case, where a depth-profile of optical constants is needed, "graded layer" models are used for this fitting. The degradation layer of thickness d is subdivided into N sublayers of equal thickness t which are considered as a mixture of two components, undamaged "bulk" and "heavily UV degraded" material. Best results are obtained when the relative volume fraction f_α of the "heavily UV degraded" material is considered exponentially graded [4]:

$$f_a(\delta) = A_s e^{-B\square\delta}$$

where δ is the normalised depth at the surface (δ=d/t), A_s is the percent conversion at the surface of the corresponding sublayers and B the decay rate of the conversion. Profiles of refractive indices of space application polymers have been produced using this methodology [4].

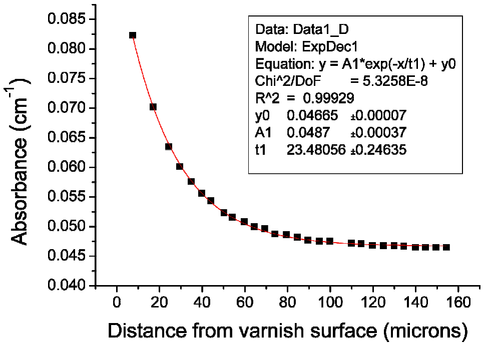

Figure 1: *Absorbance profile for dammar varnish film on glass aged for 200 hours in a Microscal (LFT1E—500) unit*

Results

The results show an exponential decrease (Fig. 1) of the absorbance from the varnish surface in accordance to previous researchers [1].

Conclusions

The optical profile of picture varnishes may non-destructively be calculated by VASE. The work will continue with optimisation of the multilayer model and also analyses of other types of varnishes (mastic, copal, paraloid B72 etc.

Acknowledgements

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POTSHERDS FROM THE INNER MONGOLIA

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Introduction

The city Khara Khoto is located in the Gobi desert in Inner Mongolia. This city was deserted in the middle of the 13th century and rediscovered in the beginning of the 20th century. Due to the isolation of the place and desert weather conditions, the city was eroded and buried by desert sand. However, over the years, lot of artefacts have come to the surface due to the windy climate. Ceramics typical for Khara Khoto have been found at the site. Several pieces of these ceramic sherds have been measured non-destructively with neutron diffraction as well as complementary synchrotron X-ray diffraction to extract information on mineral composition and the firing process of the sherds.

Experimental

Neutron diffraction measurements were performed at SPODI [1, 2], a high intensity and high resolution powder diffractometer (Fig. 1) at the Forschungs-neutronenquelle Heinz Maier-Leibnitz (FRM II, TUM, Garching).

Neutron radiation is ideally suited for the investigation of archaeological samples. The neutron penetration depth of materials is mostly large or complete in comparison to X-ray radiation which probes only the surface or very small samples by transmission. Therefore neutron radiation can be used as a non-destructive probe for archaeological samples [3].

In addition, complementary high resolution X-ray synchrotron measurements were performed on powder diffractometer ID31 [4] at the ESRF in Grenoble, using small powdered samples extracted from the sherds. This data allows due to the very high resolution of the X-ray beam further information on the mineral phases present.

Results

The sherds (Fig. 2) investigated consists of primary minerals as a part of the raw clay material before firing. Mainly mullite was detected with additional cristobalite, quartz and anorthite.

Figure 1: *Structure powder diffractmeter SPODI at Forschungsneutronenquelle Heinz Maier-Leibnitz.*

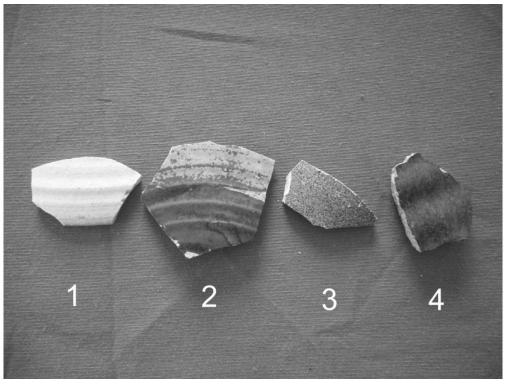

Figure 2: *Four potsherds from Inner Mongolia.*

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ARCHAEOMETRY RESEARCH OF LITHIC RAW MATERIALS FOR EARLY NEOLITHIC PREHISTORIC COMMUNITIES WITH PGAA

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Introduction

Obsidian is a favourite subject of archaeometrical studies. Radiolarite is of comparable significance for lithic assemblages in the Central and Southern parts of Europe, however, much less analyzed yet. In the earliest phase of the Neolithic, both obsidian and radiolarite are important markers of the movements of goods and people trading them. In this way, we may trace the Neolithisation process, too.

There is no local obsidian on the territory of Croatia: import, however, may originate from both the Carpathian Basin and the Mediterranean region. The importance of radiolarites is adequately demonstrated in Hungary by now. It is apparent, however, that there is essential local supply of various radiolarites in Croatia, too. In addition, there is considerable (supposed) import from the territory of Hungary. Thus, we wish to find objective discrimination features to define these supply zones and the border of these zones.

Experimental

Prompt Gamma Activation Analyses (PGAA) was applied to determine the major and trace components of the objects. PGAA was done using the horizontal cold neutron beam of 10^8 $cm^{-2}s^{-1}$ intensity at the Budapest Research Reactor. Since the neutrons can penetrate deep into the sample, the method is regarded bulk. Furthermore, because of the low intensity of neutron beam and the short lived decay products, it is absolutely non-destructive. [1, 2]

Results

Obsidian from archaeological context was provided from Croatians; fieldwork both in Hungary and Croatia supplied comparative geological samples.

After fieldtrips in Croatia and Hungary, we started to perform PGAA on the objects. We were able to quantify most major- and some trace components. The analytical results were built in our previous database of lithic material from the Carpathian Basin and surroundings. Based on the comparison between elemental compositions of archaeological obsidian from Croatia and archaeological and geological samples from other regions, it seems that the provenance of the objects can be determined with high probability. Some trace elements, like B and Cl can be significant in characterisation of different origin obsidians. With radiolarite, we have only very limited results due to low number of analyses performed as yet. We anticipate that it will be more difficult but historically equally important.

Conclusions

The non-destructive feature of the PGAA is highly capitalised during investigations of valuable archaeological pieces. The results definitely can be used for provenance study of obsidian, and hopefully for that of radiolarite, too. In order to obtain more reliable conclusions on characterisation of the object, we have to increase the number of investigated objects.

Acknowledgements

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RADIOGRAPHY DRIVEN PGAI AND NEUTRON DIFFRACTION MEASUREMENTS ON TEST OBJECTS DESIGNED FOR THE ’ANCIENT CHARM’ PROJECT

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Introduction

The aim of the ‘Ancient Charm’ project launched in 2006 by the European Commission is to reveal 3D elemental and phase images of complex museum objects by combining different neutron based techniques: Neutron Radiography/Tomography (NR/NT), Prompt Gamma Activation Analysis (PGAA), Time of Flight Neutron Diffraction (TOF-ND) and Neutron Resonance Capture Analysis (NRCA). Among these methods NR/NT gives two- or three-dimensional morphological information, PGAA provides elemental compositions; TOF-ND identifies phase distributions of metal and mineral components, both in a non-destructive way.

Experimental

As a novelty, using a collimated neutron beam and an xyzω-moving table, interesting features in the X-ray or neutron radiographies can be studied in terms of their elemental or phase compositions. Systematic sample scans, called Prompt Gamma Activation Imaging (PGAI) can be employed to obtain element maps of an object. Complex test samples, so called ‘black boxes’ (iron and aluminium walled cubes of 40 and 50 mm edge lengths, respectively, containing materials relevant for the compositions of complex archaeological objects), and imitations of genuine museum objects, so called replicas, were constructed and analyzed by these methods in order to develop and validate a routine for combined investigations.

Results

The results of radiography driven PGAI and TOF-ND on an Ancient Charm black box, and, moreover, results of PGAI on a replica are presented. With PGAI the constituents of the black box H-VI are identified, e.g.: the fibre-like material is identified as Ag chippings; Na and Cl in a molar ratio 1:1 in a section. TOF-ND has identified gypsum and talc in all sections. TOF-ND determined quartz and sodium chloride in regions, iron oxides (wuestite, magnetite) in a section. Al or Ag is difficult to distinguish by TOF-ND, but using PGAI the material is proved to be Ag. Element maps of the replica are presented. One can see that Fe is concentrated at the perimeter and Cu is distributed more uniformly in the backing.

Conclusions

According to our experiments on the objects, the methods (PGAI, TOF-ND, NR/NT) provide complementary information, none of them being sufficient alone for characterising a material. NR/NT produces high-resolution 2D/3D images that are required to survey the object for its geometrical structure and attenuation features. The contrast in the NR/NT images provides chemical and structural interpretation only if information from PGAI and TOF-ND is added. PGAI can ‘see’ the elements in the chord and/or isovolume, which is an important analysis requirement in archaeological sciences. TOF-ND is phase sensitive and can identify structures and phases, for example distinguish carbon phases and oxides in iron objects.

Acknowledgements

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P12

TOF-ND AND LIPS COMBINED STUDIES OF ANCIENT BRONZE FIGURINES

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Introduction

Time of Flight Neutron Diffraction (TOF-ND) and Laser Induced Plasma Spectroscopy (LIPS) are complementary, non-invasive techniques providing access to a wide range of information on technology and corrosion features of objects of art and historical interest. In particular, recent investigations are evidencing their significant reliability for quantitative characterization of copper alloy artifacts achieved by means of careful preliminary calibration steps.

The neutron and laser analytical approaches can get really powerful tools whenever used in integrated archaeometallurgical protocols based on the correct formulation of the knowledge-problems along with a suitable selection of the traditional techniques to be included in the study.

The deep penetration of thermal neutrons through dense matter allows achieving macrostructural information of hidden core and repair materials and statistically meaningful microstructural parameters of metal and mineral phases. Conversely, calibrated LIPS provides elemental depth profiles (up to about 2 mm in depth) and hence information on composition of surface concretions, coats, patinations, mineral stratifications, and eventually metal substrate.

Here, TOF-ND and LIPS were successfully applied to study a set of bronze figurines of Etruscan and Roman styles belonging to the antiquary collections of Florence's National Museum of Archaeology, which includes some hundreds of artifacts from private collections of the last five centuries.

The main aim of the work is to collect data for discriminating among genuine ancient productions, modern replicas, arbitrary counterfeits, pastiches other. To address such authentication tasks TOF-ND and LIPS measurements were combined with preliminary archaeological attributions and a set of traditional analyses.

Experimental

Here, we focus on two case studies: and hollow-cast figurine (height of about 30 cm) representing a man sitting on a trunk (A) and a solid-cast Venus (B).

The TOF-ND measurements were performed on two different diffractometers, INES and ENGIN-X at ISIS neutron spallation source, Rutherford Appleton

Laboratory (UK). INES was mainly used to obtain a quantitative multiphase analysis of the bulk composition of the different sculptural elements of the statuettes, while ENGIN-X was exploited to scan the inner part using relatively small gauge volumes (millimetres scale).

The portable LIPS is a homemade instrument equipped with a compact QS-Nd:YAG laser (1064 nm), optical collection system, and four compct optical fibres-coupled spectrometers covering the spectral range 200-600 nm with a resolution of 0.06 nm.

Both the techniques were calibrated using a common set of prepared samples and applied in combination with X-ray radiography, AAS, ICP-OES, XRD, and optical and ESEM metallographies of two metal samples.

Results

The phase and elemental compositions of the figurines were thoroughly analysed through Rietveld refinement of about sixty diffraction patterns and the fitting of thousand of elemental spectra using a home-made software. The later corresponds to depth profiles of about forty spot of analyses.

The most of the data of the figurine A, including depth profiles, presence of a core bar and other indicated it is very probably a fake. Whereas those of the figurine B supported the authenticity of the whole body with exception of the right arm, which was likely integrated along the last centuries. It is actually the only part, which contains zinc.

Conclusions

The work demonstrates as integrated analytical approach can exhaustively address authentication problems. Furthermore it provides evidence that in many cases objective authentications can be achieved combining bulk and surface analysis techniques, such as TOF-ND and LIBS.

Acknowledgements

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NON-DESTRUCTIVE CHARACTERISATION OF SILVER/COPPER COINS USING TOF NEUTRON DIFFRACTION

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Introduction

Non-destructive neutron diffraction on intact metallic and ceramic artefacts and metal objects was initially applied on the ROTAX instrument at the accerlerator-based pulsed neutron source ISIS using a polychromatic neutron beam (termed as the time of flight (TOF) method) [1-2], while later monochromatic neutrons at a reactor source have also been used to study ceramics [3]. Neutron diffraction can be employed to complement other established analysis methods such as metallography XRD, XRF, PNAA, EDX, and PIXE. It can deliver information on the bulk mineral or metal phase abundances, by using both the Rietveld or the Two Stage method of profile fitting [4-5].

The present work focuses on the characterisation of silver/copper coins from the Treasure collection of Gazoros (CH IX 61) in Serres Greece, using a neutron beam of large cross-section to obtain diffraction patterns from the entire sample. The measured samples were two Thassian (Ag)-hemiekto, and three (Cu-Ag) coins: two Thassian statir triti and one hemidrachmo of Neapolis, all found in a single grave. The chronological estimation based on other archaeological findings suggests that the samples were minted during the 2nd quarter of the 4th century B.C.

Experimental

The measurements were carried out using the ROTAX instrument, a medium resolution neutron diffractometer, at the pulse neutron source ISIS at the Rutherford Appleton Laboratory, United Kingdom. The samples were exposed to an incident neutron beam of 15-25 mm^2 for about 2-3 hours. Details on the experimental set-up and the TOF method are given in ref. [1]. The resulting diffraction profiles were analysed using the program Amphorae [6].

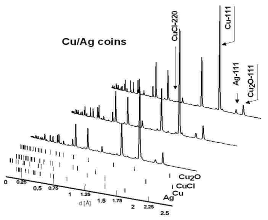
Results

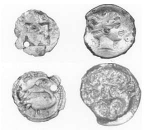
The (Cu-Ag) coins showed very similar diffraction patterns (Fig. 1a). The pronounced copper peaks originate from the core of the sample, while the smaller silver peaks result from the surface of the sample. Additional high quantities of Cu_2O and CuCl phases are also identified. In (Fig. 1b) the high amount of silver contents of the two silver coins is manifested by the prominent (111) Ag peak. A quantitative analysis of the data will be presented.

Conclusions

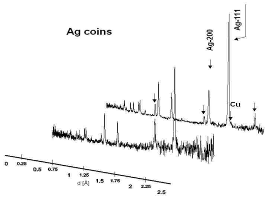
During the present study five ancient coins were examined. There is no sampling required, which is very important for objects as small as coins.

1. 2. 3.
a. (1,2) Thassian Triti 3.Neapolis hemi-drachmo





b. *Thassian Hemiekto*



c. The ND patterns of two fake triti coins (bottom), measured for comparison along with the profile of a Vergeo triti.

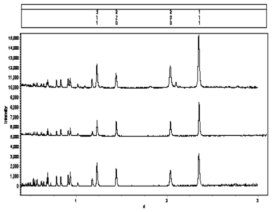


***Figure 1:** Neutron diffraction profiles of the coins.*

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P12

METHODOLOGY FOR LARGE SAMPLE NEUTRON ACTIVATION ANALYSIS OF CULTURAL HERITAGE OBJECTS

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Introduction

Large Sample Neutron Activation Analysis (LSNAA) compliments and significantly extends the analytical tools available for cultural heritage and authentication studies providing unique applications of non-destructive, multi-element analysis of materials that are too precious to damage for sampling purposes. The LSNAA method incorporates neutron irradiation of the bulk sample and subsequent measurement of the activity induced by a HPGe based gamma spectrometry system. The parameters that differentiate LSNAA from traditional NAA are the corrections needed for self-absorption of gamma rays emitted by activation products, self-shielding of the activating neutrons, sample asymmetry, the geometric volume factor and other factors [1,2,3,4]. In this work the LSNAA methodology developed in order to non-destructively analyze a ceramic vase is discussed.

Method

A painted ceramic vase (H=15.6 cm, D_{max}=11.5 cm) was analyzed. Sample irradiation was performed at Reactor Institute Delft graphite thermal neutron column Big Sample Neutron Irradiation System (BISNIS). Subsequently, measurement of the gamma activity induced in the sample was performed by a 90% efficiency HPGe detector system. Correction algorithms to account for thermal neutron self-shielding during sample irradiation, gamma-ray self attenuation and the extended source geometric factor during gamma ray counting were derived using the MCNP code. The LSNAA results were compared against conventional INAA results of sub-samples obtained from the vase.

Results

The predicted thermal neutron flux depression factor [4] taking into account the actual shape of the vase was 0.981±0.015. Moreover, the experimental determination of the HPGe detector Full Energy Peak Efficiency (FEPE) with a point-like source and a numerical correction for the source extended dimensions (including self-absorption) is shown in Fig.1. The LSNAA to INAA concentration ratio for As, Ca, Ce, Cr, Cs, Eu, Fe, K, La, Rb, Sb, Sc, Sm, W were 0.94, 0.90, 0.81, 0.85, 1.08, 0.89, 0.85, 1,85, 1.09, 1.58, 1.37, 1.36, 0.77, 1.08, respectively.

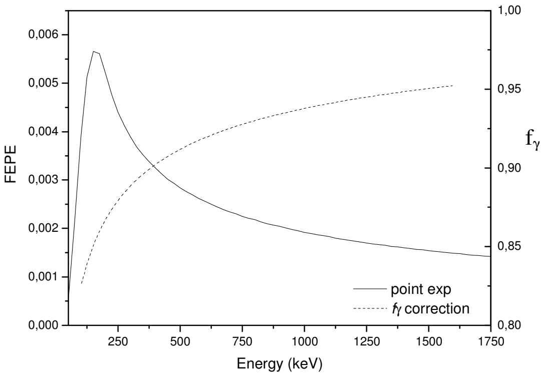

Figure 1: *Experimental full energy peak efficiency for point source and predicted efficiency correction factor,* f_γ *as a function of photon energy for the vase.*

Conclusions

Correction factors to account for neutron self-shielding, gamma-ray attenuation and volume distribution of the activity in a ceramic vase representing an archaeological object were estimated. A good agreement between LSNAA and INAA results was observed. The developed methodology responds to the requirement for a validated procedure for LSNAA of cultural heritage objects.

Acknowledgements

The experimental work was performed at Reactor Institute Delft under the support of NMI3 trans-national access program.

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STUDY OF METALLIC COMPONENTS OF HISTORICAL ORGAN PIPES THROUGH SYNCHROTRON RADIATION X-RAY MICROFLUORESCENCE IMAGES AND GRAZING INCIDENCE X-RAY DIFFRACTION

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Introduction

An organ contains flue and reed pipes constructed mostly of tin and lead spotted metals. There are no moving parts within a flue pipe organ. Reed pipes contain an additional vibrating part, the Cu-based alloy tongue that vibrates on the shallot. The tongue crucially influences and produces sounds [1,2]. In most cases, both tongues and shallots are made of brass (a copper–zinc alloy).

The composition and microstructure of historic tongues from reed pipes of a baroque organ and a modern organ were studied. The distribution and correlation of the lead and other trace elements in the two brass alloys were of prime interest. This was accomplished using a combination of laboratory techniques. New microanalytical methods employing the ID 18F beamline at the ESRF were used to obtain elemental and chemical imaging of the main phases and the trace elements at a sub-micrometer scale.

Experimental

The analysed included several samples historic tongues from reed pipes of a baroque organ and a modern brass alloy used by organ builders to make new organs.

A Siemens D5000 diffractometer with a Cu target and removable Grazing Incident Diffraction (GIXRD) device was used for the non-destructive characterisation of the crystalline phases present at the bulk and the outermost layers of the samples. µXRF mapping was performed by synchrotron radiation at microprobe station ID18F [3] on the metallographic cross-section

Results

X-ray diffraction analyses were carried out to characterise the microstructure of the old and modern alloys used to make tongues. The reflections can be indexed according to literature data [4]. The results correspond to $Cu_{0.64}$-$Zn_{0.63.}$ The modern tongue had the same composition as the old one. It also includes new phases, such as metallic lead and other phases of Cu- Zn. Quantification of these elements by EDX analysis is difficult due to the technique's detection limits. To overcome this problem, a more sensitive SR-µXRF analysis was carried out in the ID18F. The results indicate that the old historical brass tongue has a fitted elemental concentration yield of around 64%Cu and 34%Zn for the main elements. 2D mapping highlighted the presence of traces of 0.4%Pb, 0.2%Ni, 0.2%Fe, and 0.2%Sn in the bulk of the sample. The elements below 0.01% concentration, such as 0.08%As, 0.01%Se, 0.006%Sr, and 0.1%Bi, were quantified. It is interesting that the higher zinc concentration found in this tongue is similar to the organs dated around 1750 [5].

Conclusions

This study reveals the different trace elements and their localization in the phases using µ-XRF. Another important finding of this analysis was the confirmation of the role of metallic Pb in the final microstructure of the tongue. Unlike zinc, lead is not soluble in copper. This means that the lead atoms in a lead-copper melt are not equally distributed throughout the copper. These analyses show an excellent correlation between the XRD patterns of the old tongue, the quantification obtained with the PyMCA code, and the distribution of the main elements using the synchrotron-based µXRF imaging. The information obtained about the modern tongue using these laboratory techniques was sufficient for identification.

Acknowledgements

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STUDY OF JOSEFA D'OBIDOS AND BALTAZAR GOMES FIGUEIRA PAINTINGS BY μ–FTIR AND IN-SITU AND SYNCHROTRON XRF: ASSIGNING AUTORSHIP?

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Introduction

Josefa d'Óbidos is a renowned Portuguese painter from the 17th century, daughter of Baltazar Gomes Figueira, also a famous painter, who worked in Spain with Velásquez and Zurbarán. Despite the national and international recent increased interest in their work, no systematic material study of their works has ever been done and it is sometimes difficult to assign the authorship of the paintings. This is especially problematic because the two authors were close relatives that shared the atelier, and probably raw materials and the fathers influence in the daughter work is obvious (fig. 1).

Experimental

Elemental analysis was performed on 8 paintings from Evora Museum using non-destructive in-situ X-ray fluorescence spectrometry with an Amptek X-ray source Eclipse II and XR-100CR detector. Beside the small x-ray spot on the painting, the fluorescence is an average of the preparation and paint layers.

Microfragments were collected and mounted in epoxy resins. The cross-sections were observed by optical microscopy allowing the quantification and characterization of the paint layers.

FTIR spectra were obtained using a Nicolet Nexus TM670 microspectrometer giving further information about binders and pigments.

Elemental composition and compositional maps were further obtained by XRF induced by synchrotron radiation, at ANKA synchrotron using the confocal SR μ-XRF setup available at the FLUO beamline. The X-ray beam was monochromatized at 20 keV by a W/B4C multilayer monochromator and focused by Compound Refractive Lens.

Results

The major element composition in the paintings of Josefa d'Óbidos and her father are very similar (fig. 2), suggesting that the two painters used a similar palette composed by vermillion for the reds, ochre for yellows and browns, azurite and smalt for the blues, white lead for white, carbon for blacks and copper pigments for the greens

The optical microscope observations show that the imprimituras are completely different in color although mainly composed by calcite, silicates and oxide minerals, with red ochre more abundant in the paintings of Baltazar and brown ochre in Josefa artwork. The μ-FTIR reveals that the binder in Josefa oeuvres is composed by oil with varnish whereas for Baltazar is only oil. White lead and kaolin are present in all preparation layers but in the case of Baltazar it also presents chalk and gypsum.

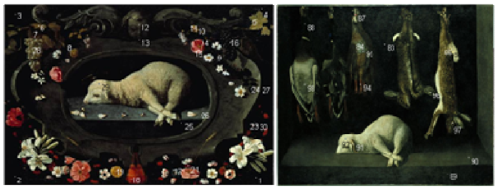

Figure 1: *"Agnus dei" and "natureza-morta com cordeiro e peças de caça" by Josefa d'Óbidos and Baltazar Gomes Figueira, respectively.*

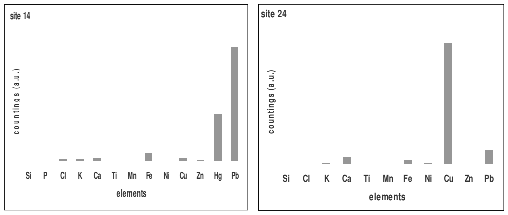

Figure 2: *In-situ XRF of a red area and a green area*

The low detection limits of synchrotron XRF led to the discovery of trace element fingerprints that underline some differences in the same pigments. Furthermore, the microprobe characteristics of the technique allowed sketching chemical profiles of the cross-sections and appreciating the technical details of the painters.

Conclusions

Josefa d' Óbidos and Baltazar Gomes Figueira used the same pigments that have some distinct trace fingerprints. Technical differences between the two painters are revealed by the optical study of cross section and compositional profiles.

COMPOSITION OF ROMAN MURAL PAINTINGS FROM SOUTHERN PORTUGAL: SOURCES, COLOUR AND CONSERVATION

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Introduction

The Southern Portugal was inhabited by populations with different cultures that left their cultural and historic legacies. One of these cultural remnants is the mural paintings (“frescoes”) that are widely disseminated by rural and urban civil and religious buildings of the region. This technique was initially implemented by the Romans that occupied the territory during several centuries.

Experimental

The mural paintings from the Roman building (4th/5th century) in Rua dos Burgos (Evora, Portugal) and Mirobriga archaeological site (Santiago do Cacém, Portugal) were the case studies. The main pigments are yellow and red and also important are white, blue and green pigments.

Elemental analysis was performed by non-destructive in-situ XRF using an Amptek X-ray source Eclipse II and XR-100CR detector. The fluorescence signal is a averaging of preparation and paint layers but the capability to identify the composition of pigments are remarkable.

Elemental analysis of the pigments in cross-sections was carried out using the confocal SR μ-XRF setup available at the FLUO beamline. The X-ray beam was monochromatized at 20 keV by a W/B4C multilayer monochromator and focused by Compound Refractive Lens. The polycapillary is required by the confocal geometry and allows obtaining elemental composition and mapping.

Results

The results show that the pigments are from natural sources. For instance, the red pigments have a natural origin marked by the presence of elements as Ti or Mn (fig. 1). The presence of high proportion of opacifiers like calcium or lead presupposes that the concentration of pigment in the ochre is very high. This means that the Romans had the technological capacity to separate and concentrate the pigment (iron oxide) from silicates and other oxides that occur naturally together.

The mapping capacity of FLUO beamline allowed the study of the position of different elements on cross sections of the frescoes (fig. 2). Some elemental associations and segregations are obvious.

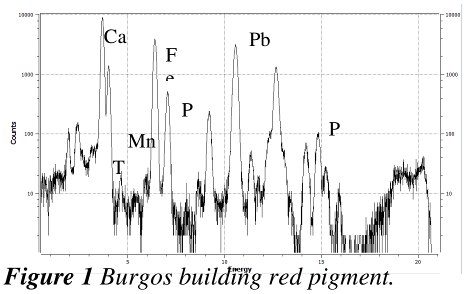

***Figure 1** Burgos building red pigment.*

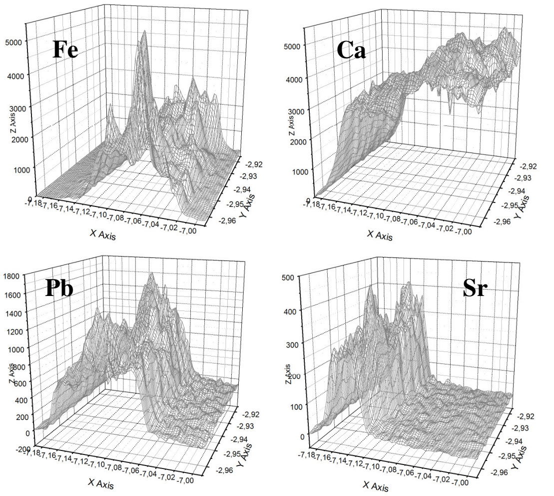

***Figure 2:** Compositional mapping in a cross section of a roman fresco. The x axes is perpendicular to wall, the area enriched in Ca is a preparation layer.*

Conclusions

Although the same type of pigments had popular use up to the 20th century, the natural pigments never were so pure [1] because after the decline of Roman Empire this high technical ability was not achieved until the emergence of synthetic pigments.

Acknowledgements

The experiment was supported by the EC Integrated Infrastructure Initiative “I3 IA-SFS” and EEA Grants. The authors wish to thank Rolf Simon for his support during the measurements.

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EVALUATION OF CONSOLIDATION TREATMENTS ON WATERLOGGED ARCHAEOLOGICAL WOOD BY MEANS OF SYNCHROTRON LIGHT X-RAY MICROTOMOGRAPHY

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Introduction

In favourable waterlogged conditions, characterised by of low temperature and low oxygen concentration, archaeological wooden artefacts, such as shipwrecks, can survive in relatively good state of preservation. Nevertheless, as a result of the action of *biota* among which the anaerobic bacteria, waterlogged wood is often deeply degraded and has undergone loss of polysaccharidic components (cellulose and hemicelluloses). This process imply the increase, under ageing, of porosity and, thus, of water content of wood, which can rise up to 1000% in dried weight.

Conservation treatments of archaeological waterlogged wood artefacts are very often expensive and technically difficult. They often involve the replacement of water with substances which, fill the most of cavities -even of those created in the cell walls- preventing collapses and stresses during drying [1]. The effectiveness of each treatment strongly depends on the chemical and physical characteristics of such substances and, moreover, on their degree of cavities-filling, penetration depth and distribution in the wood structure.

Experimental

The deposition of ten types of substances, and their mixture, in archaeological wood samples (pine and elm) was investigated by synchrotron radiation X-ray microtomography (SR-μCT). Tomography experiments were performed at the ID 19 beamline of European Synchrotron Radiation Facility (ESRF) in Grenoble (France) [2].

The examined treated wood samples were prepared in the frame of a project for the experimentation of products and methods for the conservation of degraded waterlogged wood artefacts, coordinated by the Archaeological Superintendence of Tuscany (Florence, Italy) and aimed to the conservation of wooden objects and shipwrecks recovered in the archaeological site of the Ancient Ships of San Rossore (Pisa).

Results

X-ray microtomography allowed to investigate in 2D and in 3D the internal structure of wood samples in a non-destructive way. The imaging permits to highlight wood morphology with good detail (≈1μ) and to localise the impregnating substances in wood cavities at different depth from the external surface (Figure 1).

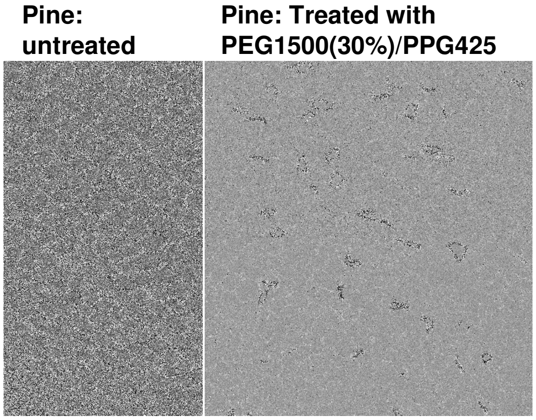

Figure 1: *SR-μCT images of archaeological pine wood from S. Rossore site, before and after impregnation with a mixture of polyethylene glycole (PEG) and polypropylene glycole (PPG).*

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LASER CLEANING OF AGED SHELLAC FROM WOOD

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Introduction

In this work we focused in the investigation of the removal of Shellac, a typical coating used on historical wooden artifacts. Shellac coatings often lose their elasticity and mechanical strength when exposed to environmental parameters such as UV light, temperature and RH. Moreover, they lose their glossiness and transparency and become hard and insoluble. The common cleaning procedure for shellac in conservation involves the use of laborious mechanical methods or the use of potentially hazardous solvents [1]. As lasers are now routinely employed for the removal of organic coatings from various substrates of cultural heritage objects [2], this study aimed to identify whether lasers could be applied in the removal of shellac [3].

Experimental

Hardwood and softwood boards were coated by one layer of shellac on the tangential surface, and a thickness between 25 μm to 35 μm. Two Nd: YAG (1064 nm) and two excimer (248 nm) laser systems, emitting pulses of nanosecond (ns) and picosecond (ps)duration at each wavelength, were used to determine the optimal laser parameters [2]. Etch depth measurements were performed by the use of a mechanical stylus profilometer (resolution of 200 vm). Optical microscopy (OM) and Scanning Electron Microscopy (SEM) performed in order to estimate structural and chemical alterations of wood, in extreme cases of laser fluence. The minimum laser fluence for the removal of shellac and for the damage of uncoated wood was determined in order to asses the so called “self limiting effect”.

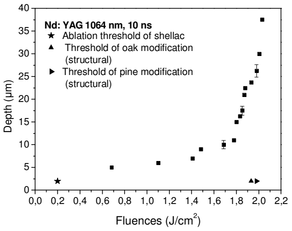
Results

In summary, it was revealed that at 1064 nm (Fig. 1), the self limited window was wider than that observed at 248 nm for both pulse durations. Furthermore, with ps pulse durations a narrower self limited window was obtained than with ns pulses at both wavelengths applied.

Conclusions

The result of laser ablation test indicated that it is sufficient to remove shellac resin from wooden surfaces without affecting it. The fact that the ablation threshold of shellac and that of wood (softwood and hardwood) have cross differences of several magnitudes is setting up the self limited parameters for the laser cleaning procedures. Best result achieved with the Nd YAG ns laser.

Ablation rate with Nd:YAG laser



SEM result with Nd :YAG laser

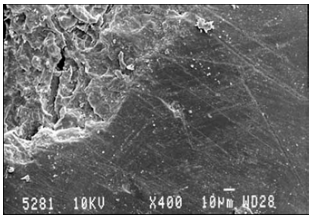


Figure 1: *a) Ablation rate of shellac when irradiated with Nd: YAG1064 nm, (pulse duration 10 ns). Every datum point is an average of at least 3 to 4 different measurements. The error bars are indicative. b) SEM micrograph of spot created (arrowed) on oak coated with shellac with 1 pulse. Fluence: 0.2 J/cm2. Laser: Nd:YAG 1064 nm, 1 ns. Bar = 10 μm.*

Acknowledgements

The authors gratefully acknowledge Prof C.Fotakis for his scientific support to the realization of this project, as well as Ms Aleka Manousaki for her assistance with the SEM.

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P18

AN EVALUATION OF REFLECTANCE-ABSORPTION INFRA RED SPECTROSCOPY FOR IN SITU INVESTIGATION OF ORGANIC COATINGS ON CORRODED METALS

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Introduction

Reflection-Absorption Infra Red Spectrometry (RAIRS) along with Attenuated Total Reflectance spectroscopy (ATR) has been widely used as a characterization and monitoring tool that can be used to evaluate the effectiveness of coatings on metal [1]. Increasingly, these techniques are being applied to test coatings for cultural property made of metals, such as for outdoor bronze monuments [2]. The advantage is that RAIRS can carry out an in-depth characterization of layers from the bulk coating to the metal surface analyzing the variations in the chemical bonds. However, for an accurate interpretation of the spectra throughout the layers, the following properties are significant: thickness and uniformity of the coating, glossiness of the surfaces and nature of the metal surface. Our problem is that for conservation research the effectiveness of coatings often needs to be evaluated on corroded metals. This paper evaluates the application of RAIRS to investigate Paraloid®B-72 and Poligen ES 910009® coatings of variable thickness on corroded iron and copper alloy coupons under the auspices of the EC project PROMET. Furthermore, it highlights how a simple FTIR system (PE Spectrum GX) can be adapted to carry out reflectance measurements coupling with a reflectance accessory (PE, 12.5° fixed angle) at a relatively low cost. Such adaptability makes it attractive for conservation research, since most Conservation facilities, such as ours have a simple FTIR system.

Experimental

A description of how the corroded iron and copper alloy coupons were prepared, aged as well as the nature of these two coatings, their application and testing is given in detail elsewhere [3]. A series of approx. 100 copper and iron alloy corroded coupons coated with Paraloid® B72 and Poligen® ES91009, both artificially and naturally aged, were tested using KBr FTIR and RAIRS. Some model coupons were prepared as ideal (polished with uniform coating thickness) to compare the results to the coated corroded coupons.

Results and Discussion

The most interesting results were found for the new coating Poligen®ES91009 showing strong carboxylic acid and carboxylate ion features in transmittance mode. Significant changes were observed in reflectance mode, most notably the new band at 1605 cm^{-1} (in Cu alloy, stronger in artificially aged coupons), and the sharp decrease (coatings on both alloys) of the original 1535 cm^{-1} carboxylate band (Fig.1). These features were correlated with those in model coupons incorporating the same coating materials with controlled film thicknesses and surface glossiness. Thus, our examination of infra-red RAIRS bands for the coated corroded coupons is entirely attributed to chemical changes.

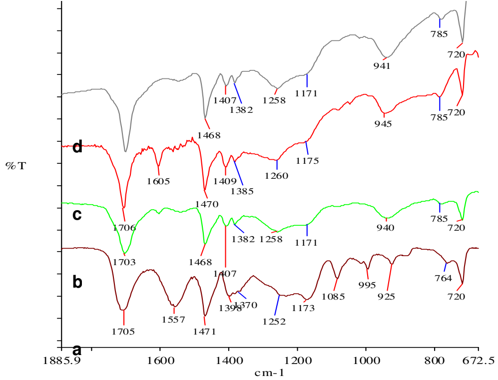

Figure 1: *Infra-red spectral features of Poligen® ES91009 films on (a) silicon wafer (transmittance reference spectrum); (b) Cu alloy coupon naturally aged (9 months); (c) bronze coupon artificially aged (chamber 30 days); and (d) iron coupon artificially aged; (b)-(d) are RAIR spectra.*

Conclusions

RAIR spectrometry was able to distinguish between chemical and physical phenomena in tested organic coatings, Paraloid® B72 and Poligen® ES91009 on corroded iron and Cu alloy coupons. Thus, RAIR can be effectively applied to detect chemical deterioration of coated surfaces of metal museum objects.

Acknowledgements

This work was financially supported by PROMET European 6th FW funded project www.promet.org.gr.

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CHARACTERISATION OF FOXING STAINS IN XVI-XIX CENTURY DRAWINGS USING μ-EDXRF

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Introduction

Foxing, a chromatic alteration of cellulosic materials is a complex phenomenon, not yet well understood. The term is applied to stains of reddish-brown, brown, or yellowish colour, generally of small dimensions, with sharp or irregular edges, most of which, if excited with UV light, show fluorescence [1]. The formation mechanisms of foxing have been studied since 1935, however, despite more recent intensive research since the 1980s there are still no conclusive results. Some authors found evidence of bacterial and fungal growth in some foxed areas sometimes associated with the presence of iron and/or heavy-metal-induced degradation of cellulose and sizing materials. The chemical nature of foxing stains can be investigated by means of instrumental techniques such as Fourier transform infrared spectrometry, UV fluorescence, X-ray analysis [2]. In the present work, foxing stains from 32 drawings from the XVI and XIX century belonging to the collection of the Museu Nacional de Arte Antiga in Lisbon were studied by Energy Dispersive X-Ray Fluorescence (EDXRF) in order to try to find a common trend for a better comprehension of this phenomenon. The stains were also observed under natural and UV light in order to show the drawings differences in size and in the dimension and intensity of their foxing stains.

Experimental

Thirty-two drawings from the XVI and XIX century were analysed in situ with a μ-EDXRF Spectrometer. The drawings had in common severe foxing stains. Details on the experimental set-up are given in ref. [3]. Quantification of the elemental content was performed using the compare mode model of WinAXIL software (Analysis of X-ray spectra by Iterative Least-squares fitting) by IAEA. Foxing stains on drawings were observed on a photographic column stand using daylight and using a UV Waldmann W portable lamp with two Philips TL 4W/08 F4 T5/BLB.

Results

When observed under UV light, the examined stains were surrounded by a fluorescent ring.

The elemental content of the paper region of drawings was compared with the regions containing foxing stains. An increase of K was observed together with a decrease of Cl in the foxing stains (Fig.1).

Conclusions

A combination of two non-destructive techniques was applied to the study of the characterisation of foxing stains in papers used for drawings. UV light helped in the identification of the foxing stains present in the drawings. The results obtained by μ-EDXRF have been already observed in [4].

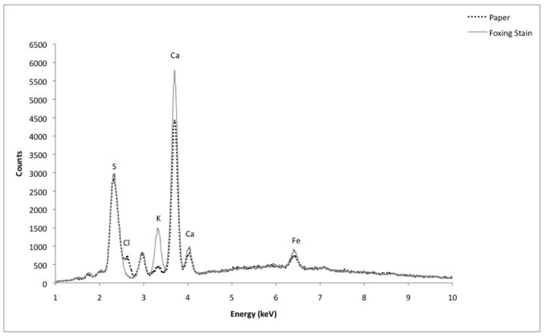

Figure 1: *Paper and foxing stain elemental content comparison.*

Acknowledgements

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P20

ANALYTICAL CHARACTERIZATION OF POLYMERS USED IN CONSERVATION BY ATR-FTIR SPECTROSCOPY

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Introduction

In the last decades there are many new polymers used in Cultural Heritage Conservation [1,2]. Among the mostly used ones are polyolefines, polyesters, polyamides, polyacrylates and polyvinyls. Their practical application depends on their composition and processing (foam, film, pressure sensitive adhesive, etc.) [3]. Some of them are used in restoration and another in exhibition, storage and transport of works of art [4]. In any case, it is absolutely necessary to know their composition: polymer or polymers and additives. There are in the market many different materials which have been manufactured for another uses but that also are been using in conservation and restoration. Usually the technical information provided by the manufacturer is not complete, so is necessary to make an analytical characterization. FTIR spectrometry is largely used for polymers identification and more recently ATR – FTIR is given excellent results [5]. The present work aims to analyze different synthetic materials which are used in conservation and restoration of cultural heritage.

Experimental

FTIR spectra were recorded using a Termo Nicolet 380 spectrometer (64 scans; 4 cm-1), equipped with an attenuated total reflection diamond crystal accessory.

The analysed samples include adhesives, coatings, pockets, non-woven fabrics, supports and foams. Some of them are composite materials and another one contains additives.

Results

The figure 1 shows ATR-FTIR spectra of DuPont Tyvek ® tape. This pressure sensitive tape is used to binding folder spines, performing book repairs to battered books, as well as a variety of other uses. It has been analyzed by both sides: support and adhesive.

The support spectrum shows a clearly correspondence whit reference spectrum 2 –polyethylene- (x). The adhesive spectrum shows absortion bands which corresponds to reference spectrum 1 –polybutylacrylate-(*) and support characteristics traces.

Conclusions

ATR-FTIR offers the advantage to obtain results fast and without previous sampling. Because of superficial analysis it is necessary realize the experiment by both sides of the materials.

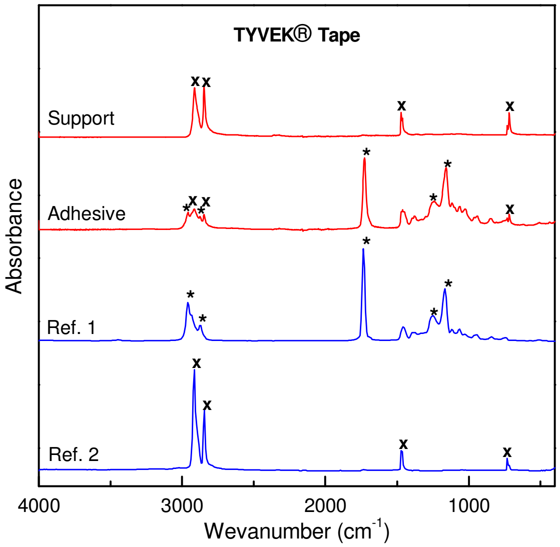

***Figure 1:** ATR-FTIR spectra of both sides Tyvek® tape and reference spectra.*

Acknowledgements

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ASSESSMENT OF GASEOUS AND PARTICULATE MATTER POLLUTANTS IN A BRAZILIAN MUSEUM

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Introduction

The assessment of damage to indoor cultural heritage, in particular by pollutants, is nowadays a major and growing concern for curators and conservators. Nevertheless, although many museums have been studied in Europe [1], the effects of particulate matter and gaseous pollutants in museums under tropical climate and with different economic realities are still unclear. An important portion of the world's cultural heritage is currently in tropical countries where both human and financial resources for preserving museum collections are limited. Hence, our aim is to assess damage and to estimate threshold values at which it occurs in hot and humid environments where air quality and microclimatic condition differences can cause deteriorations in work of art. Particulate matter as well as gases was collected at Oscar Niemeyer Museum (MON), in Curitiba, Brazil, where a large modern and contemporary works of art are displayed.

Experimental

Size segregated aerosol samples were collected for analyses of bulk and single particle elemental and molecular compositions. They were analysed by electron probe micro-analysis, utilising facilities for low-Z element determination, and by energy-dispersive x-ray fluorescence, to investigate the elemental composition of individual particles and bulk samples, and by aethalometer, to elucidate the molecular composition. The concentrations of BTEX, NO_2, SO_2, O_3, acetic acid and formic acid were assessed using passive diffusion tubes. BTEX were analyzed by gas chromatography–ion trap mass spectrometry and other gases by ion chromatography.

Results

Most of the concentrations found for the pollutants were bellow recommended exposure values (NO_2 8.1 µg m^{-3}, SO_2 0.57 µg m^{-3}, O_3 2.2 µg m^{-3}, average values). The BTEX concentrations were similar to those found in another museums, except the o m + p xilen (16.6 µg m^{-3}) and o-xilen (38.5 µg m^{-3}) concentrations, which were affected by the painting of a room near the sampling site. The concentrations for particulate matter bulk analysis inside the museum were smaller of those found outside, and the average value for those particles considered most aggressive, S-rich, Cl-rich and Fe-rich, were bellow 60 ng m^{-3}. The single particle analysis revealed that the relative abundance of particles, such as organic particles, soot, Fe-rich particles and $CaSO_4$, was similar to those found in other museums of Europe and United States.

Conclusions

The potential damage to museum collections caused by gaseous air pollutants like SO_2, NO_2, O_3, acetic and formic acid, benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as by particulate matter, were examined systematically for the first time in tropical country.

These gases and particulate matter assessed were then compared with the concentrations obtained for the same pollutants in others world museums and with some reference values provided by international cultural heritage conservation centers.

Some preventive conservation action suggestions were made, when thought necessary, based on the pollutants concentration found inside the museum

Acknowledgements

The authors are very grateful to the Oscar Niemeyer Museum direction.

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STUDY OF THE MORPHOLOGY OF IRON GALL INKS USED IN THE COPY-PRESS PROCEDURE

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Introduction

James Watt's invention of copy press in the 1780s enabled professional bodies as well as individuals to keep copies of their outgoing mail bound in books, for record purposes. The various inks used at that time were made by simple ingredients, such as gall nuts and vitriol, hence their name Iron Gall Inks, and were even manufactured at home. The various ingredients added in order to produce a better quality ink varied dramatically between recipes. In today's time, iron gall ink corrosion is the cause of one of the most drastic decompositions of a paper substrate.

The ultimate aim of this research is to distinguish between different types of iron gall ink based on their morphology with the help of Scanning Electron Microscopy. Specifically, the first step is to determine whether the morphology of an iron gall ink remains the same even after the ink has undergone the stressing copy procedure.

Experimental

As original manuscripts are invaluable, written samples were prepared in the laboratory: Eight different iron gall inks were manufactured according to recipes of that era. The recipes included the four basic ingredients that form iron gall inks -water, crushed galls, iron(II) sulphate, gum arabic- as well as additives such as glycerine, wine, silver nitrate and clove. No colourants were added. 1/2mm thickness nib was used for applying the ink on the papers and four different writing papers were employed. The writing papers were both of good and lower quality. The hydrating technique applied for the copying procedure was one of those used in the original process, namely the copy paper being wetted before it came in touch with the writing paper. All the written and copied samples were photographed in the visible area of the spectrum.

The non-copied and the copied samples were put onto carbon tabs and metal stabs and were gold/palladium coated. High magnifications were thus achieved and enabled us to have different magnitudes of the surface morphology.

Results

The study of the surface morphology of each of the eight inks revealed the diversity of the surface formations. When applied on paper, each ink produced a different surface morphology compared to the others, which enabled good distinction between inks. The experimental data of all four papers were compared to each other in order to prove that an ink's morphology is consistent independently of the writing papers used. The same process was repeated for the inks on the four writing papers after the copy press procedure. In this case two of the inks' morphologies were similar to others possibly because the ink was deformed due to the stress of the copying procedure. In most cases though, the surface morphology of the non-copied and the copied ink on writing paper remained the same, thus enabling the distinction of particular ink recipes.

Conclusions

The surface examination of eight iron gall inks manufactured from different recipes showed that the distinction of different inks is possible based on their surface morphology. Further research is underway in order to study whether these morphologies can also be reproduced and found on the thin copy paper.

Acknowledgements

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CHARACTERISATION OF PARTICULATE MATTER IN MUSEUM ENVIRONMENTS BY SPECTROSCOPIC AND IMAGE ANALYSIS TECHNIQUES

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Introduction

The quality control of indoor environment is essential for museums, galleries and sheltered archaeological sites, since it has a strong impact on the preservation of their collections. The deposition of particulate matter (PM) can initiate and/or accelerate the physical and chemical degradation of materials, while soiling affects the aesthetic values of artefacts [1]. It is therefore imperative that the size, distribution and chemical composition of PM to be identified, and suitable action to be taken in order to control their levels.

In this context, the present work studies the chemical and morphological characteristics of particulate matter collected at the National Glyptotheque of Greece, in Athens, as well as their distribution and accumulation rate. National Glyptotheque is located at an area considered as typical of moderate urban pollution .Although special care has been taken to minimize the levels of particulate matter in the exhibition area of the museum, through the installed HVAC system, the monitoring and characterisation of the PM loading is critical for planning further protective and remedial actions.

The results are correlated to the preservation and the weathering patterns identified on the indoor and outdoor sculptures and therefore, this study makes a contribution towards the challenge of many museums to keep their collections in suitable conditions and forecast problems ahead.

Experimental

Particulate matter samples were collected both, indoors and outdoors through precipitation on neutral, carbon adhesive discs for scanning electron microscope (SEM). For the indoor environment, the accumulation was monitored for 12 months, while outdoor measurements concerns the material accumulated at 4 different environmental conditions for a period of one week.

Samples were analysed in a scanning electron microscope coupled with an energy dispersive X-ray analyser (SEM/EDX) in order to study the micro-morphology and determine the chemical composition of the particulate matter [2]. The above results were compared to those derived from the mineralogical characterisation by X-ray diffraction (XRD) of the total deposition in a neutral container.

SEM photomicrographs were further elaborated using an image analysis software for extracting quantitative data on particle distribution and accumulation rate [3].

Results

The samples contained a mixture of anthropogenic and industrial aerosols, along with some mixed conglomerates, which differ in size, shape and chemical composition. Considerable differences were observed in the morphology of particles sampled at different height, while their accumulation rate was mainly depended on the location of the sampling area. The number of visitors had an impact on the accumulation rate of soil particles indoors. Finally, the design parameters of the HVAC system minimised the dispersion of outdoors PM in the exhibition area.

Conclusions

The main difference observed between the chemical composition of particles collected indoors and outdoors concerns the amount of sulphur and sodium chloride compounds. Fine outdoor particles present the highest sulphur content, while silicon and calcium are the major elements in the medium and coarse particles. Other abundant elements are chlorine and iron. The number of organic particles is small, while the study of the conglomerates formed indoors has confirmed the presence of gypsum and sodium sulphate.

Finally, the deposition of clay particles on the bronze sculptures outdoors enhances the absorption of gas pollutants like sulphur dioxide (SO_2) and nitrogen dioxide (NO_2), serving as nucleation sites for these gases and thus, accelerates their deterioration rate.

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RAMAN SPECTROSCOPY AFTER ACCELERATED AGEING TESTS TO ASSESS THE ORIGIN OF SOME DECAYED PRODUCTS FOUND IN REAL HISTORICAL BRICKS AFFECTED BY URBAN POLLUTED ATMOSPHERES

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Introduction

Bricks, together with stones and mortars, can be considered as one of the most important building materials that constitute our Built Heritage. Numerous factors which cause several decaying pathologies in bricks can be listed, but it should be emphasised that the most important and damaging one is the wet/dry deposition of combustion and greenhouse gases (CO_2, SO_x, NO_x mainly). For instance, after the impact of CO_2 and SO_x the decayed products promoted in bricks are carbonates and sulphates. Examples of the real formation of these decaying salts can be the presence of calcite and gypsum ($CaSO_4{\cdot}2H_2O$)/anhydrite ($CaSO_4$) in bricks from a historical house in Agurain (Spain) [1] following a wet deposition mechanisms. Once identified all these kind of salts in real samples, it is necessary to make sure that the aggressive atmospheric conditions are sufficient to promote the formation of these kinds of salts. Therefore, accelerated exposure test are a good alternative, in order to simulate the formation of these decayed compounds and to predict the reactions that promote the decaying mechanism.

Experimental

Nine brick batches consisting of 10 samples each one were manufactured at four different firing temperatures (875, 900, 950 and 975 ºC) following ancient methods (wood frame and/or pressed). These samples were subjected to 5 humidity/dryness cycles and 5 freeze/thaw cycles. After that, CO_2 ageing test was conducted in a chamber at controlled humidity atmosphere with a constant flux of CO_2 and later, SO_2 ageing process was conducted in a Kesternich chamber (KESTERNICH DIN 50018).

The characterisation of each sample was based on the use of Raman spectroscopy (Renishaw RA 100 spectrometer). Also ionic chromatography was used to confirm quantitatively the carbonate and sulphate concentrations after each ageing test.

Results

Thank to the non-invasive analysis by Raman spectroscopy we were able to identified the original composition of bricks as a mixture of silicates and iron oxide red (Fe_2O_3) with rutile (TiO_2) presence. After the humidity/dryness and freeze/thaw cycles, it was possible to identify the presence of calcium hydroxide and traces of calcite ($CaCO_3$) in few samples. Subsequently, in the samples exposed to CO_2, calcium carbonate was identified in the outer and inner parts of the bricks. Moreover other kind of carbonates, such as natron ($Na_3CO_3{\cdot}10H_2O$) and potassium carbonate (K_2CO_3), were also identified. Finally, after the KESTERNICH test gypsum alone or in combination with calcite was identified in the outer parts of the samples, while calcite was the only decaying product found in the inner parts.

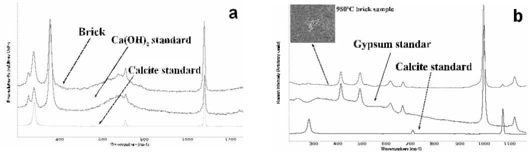

Figure 1: *(a) Raman spectra of a brick sample before CO_2 exposure (b)Raman spectra of a brick sample (950ºC) at the end of KESTERNICH test.*

Conclusions

Molecular speciation by Raman monitoring of brick samples (manufactured following ancient methods) subjected to different accelerated ageing tests was used to understand the decaying mechanisms which promote the formation of carbonate and sulphate salts in historical bricks affected by urban polluted atmospheres. The steps leading to the formation of such salts are the followings: (i) hydration of the oxides present in bricks to form their respective hydroxides (ii) reaction between the hydroxides and the CO_2 to form the corresponding carbonate, and finally (iii) reaction between each kind of carbonates with SO_2 to originate their respective sulphates.

Acknowledgements

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MICRO-DESTRUCTIVE TOOL FOR DAMAGE ASSESSMENT OF FIBRE DEGRADATION IN 15-17th c. HISTORIC TAPESTRIES

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Introduction

Flemish 15th-17th century tapestries belong to the most valuable testimonies of European cultural heritage, although most of them are actually in a very bad state of preservation. Condition evaluation often still relies on visual observations, mostly considering macroscopic physical degradation aspects and discoloration.

The aim of this study was to elaborate a micro-destructive tool for the damage assessment of the protein fibers before actual breakdown of the material becomes visible.

Experimental

Alterations in the amino acid composition of protein fibers are indicative for protein degradation at molecular level.

The efficiency of calibrated amino acid analysis by liquid chromatography with fluorescence detection as a monitoring system for both keratin as fibroin protein degradation was studied.

A practical model with new and accelerated aged reference samples [1] was developed and will be confronted with data from historic fibers.

Results

Specific ratios of amino acids, which are sensitive to change have been identified and will act as damage assessment markers, in a similar manner to identified amino acid ratios in collagen-based materials [2, 3].

For keratin, cysteic acid, tyrosin and a parameter based on the general shift of the basic and acidic amino acids (Keratin Oxidation Factor) could be defined as markers for the oxidative breakdown, while the defined degradation marker for fibroin is tyrosin.

The confrontation of the historic samples to the developed model for oxidative degradation of wool and silk proteins, showed the same tendency of degradation of the historic samples as found in the model references, revealing an even more pronounced state of degradation of the historic fibres.

Differences in degradation can be distinguished between samples from different tapestries, restoration threads and fibres taken from the front or backside of a tapestry.

Conclusions

Monitoring alterations in amino acid composition is found to be an efficient, objective micro-destructive tool for the damage assessment of protein fiber degradation at the molecular level.

The defined early warning markers, allowing objective condition evaluation of the oxidative degradation of historical tapestries, are also applicable for pertinacious textiles in general.

Acknowledgements

This research was initiated and mainly supported by the EC through the project Monitoring of the Damage in Historic tapestries (EVK4-CT-2001-00048).

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PLASMA REDUCTION OF BRONZE CORROSION LAYERS FORMED UNDER ACCELERATED AGEING CONDITIONS

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Introduction

The archaeological and artistic value of objects of copper alloy found in archaeological sites makes their preservation of primarily importance. The soil properties are determining for the degradation of the artefacts but in the case of metal bronze objects, humidity and chlorides are key factors too [1]. The application of hydrogen plasma [2,3,4] on corroded Cu–based bronze alloy coupons has been studied. Coin like coupons [5] with chemical composition and metallurgical features similar to those of ancient alloys were used to create corrosion layers almost similar to the ones produced during the burial of the bronze objects.

Experimental

The coupon surface was corroded in two stages, firstly by chemically attacking it to initiate a corrosion layer and secondly by burying it in soil with humidity to help its corrosion by the soil constituents. As-prepared coupons were examined on the surface and on the cross-section by optical microscopy, metallography, X-ray diffraction, scanning electron microscopy and microanalysis.

Hydrogen plasma has been employed to reduce the as-formed corrosion layers on the patina of bronze objects and stabilize the surface, and/or remove soil layers embodied on the corrosion layers. The newly reduced surface by plasma was again characterized in order to check on its' final condition. The reduction depth has to be controlled as not to change the patina layer on the surface of the metal, so that the pleasing and partly protective patina not to be removed from the object.

Results

The complete removal of the large amount of the basic copper tri-hydroxychlorides that were introduced to the surface of the specimens by chemical corrosion is practically impossible, despite that longer treatments at higher temperatures can be more effective but not recommended, because they can eventually affect the integrity of the treated object. The plasma treatment at all conditions is successful by decreasing the density of the corrosion products and, therefore, facilitates subsequent mechanical cleaning. The gradual elimination of the chloride containing corrosion products in favor of the formation of more stable species and sometimes even the complete reduction back to copper metal is proportional to the duration of the plasma treatment.

There is an indisputable change in the original color of the samples. The color monitoring of the treated samples in all cases revealed that the initial dark brown color of the shorter treatments eventually turns to more shiny red at longer treatments, due to the formation of cuprite and the subsequent reduction back to copper metal.

Apart from the aesthetic reasons that should be considered there is also a question about the stability of the newly formed surface. This technique should be considered as a good practice for the removal of the soil agglomerates and the free-chloride corrosion products from objects with warty corrosion, as the encrustations become brittle and can be quite easily removed mechanically in order to clean down to the level of the rest of the patina. It should be taken into account that, when the corrosion layer contains chloride species, this process should be followed by complementary treatment, which will properly isolate and seal the surface from any contact with air and moisture.

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SPECTROSCOPIC AND THERMOANALYTICAL STUDY OF WOODEN SAMPLES DISINFECTED AND CONSOLIDATED BY IRRADIATION

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Introduction

Wood artefacts conservation by gamma irradiation is a relatively new technique with perspective of increased utilization. Disinfection and consolidation of samples could be done at the same time. The FTIR, FT-Raman and TGA-IR techniques were used to detect changes in wood structure after conservation treatment. Vibrational spectroscopy techniques were used to identify wood type, biological decay and weathering state.

Experimental

Wooden samples of sycamore maple and pine, older than 300 years, collected from three Romanian churches were studied. The consolidation and disinfection was done by impregnation and radiation polymerization of a styrene unsaturated polyester tetrahydrophtalic resin [1].

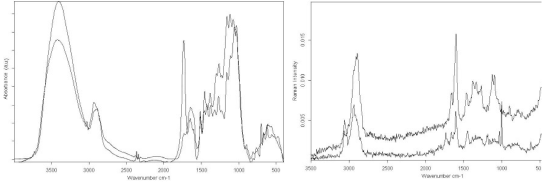
Bruker Vertex 70 class FT-IR spectrometer equipped with a fiber optic mobile RAMPROBE attached to RAM II module (LN2 Ge detector) and TGA-IR external unit as detector for NETZSCH STA 409 PC Luxx simultaneous thermal analyzer was used. FT-Raman spectra were recorded between 50 and 3500 cm^{-1} using Nd:YAG laser (1064 nm, 1-500 mW). Spectral acquisition was made with 100 scans at a 4 cm^{-1} resolution. *In situ* measurements were made directly on the wood surface. FT-IR spectra were recorded in KBr pellets [1]. Vector normalization of the spectra on the whole frequency range was done.

TGA-IR coupled technique was used to correlate biological decay of wooden samples with pyrolysis products from investigated samples.

Results

FTIR spectra show differences in band intensity and position for various wood types. The relative change in the ratio lignin/carbohydrate reference bands was used to assess the biological decay. After irradiation a strong band at 1732 cm^{-1} appears indicating the presence of ester groups (Fig. 1). Shifts in band position and intensity of wood spectra indicate changes at molecular level by cross-linking.
In the FT-Raman spectra the polymerization process is evidenced by the presence of new bands at 1734 cm^{-1} and 1002 cm^{-1} and various changes in intensity and position of other peaks.

Thermal analysis shows a thermal stability improvement after impregnation and irradiation polymerization (figure 1).



FTIR spectra FT-Raman spectra

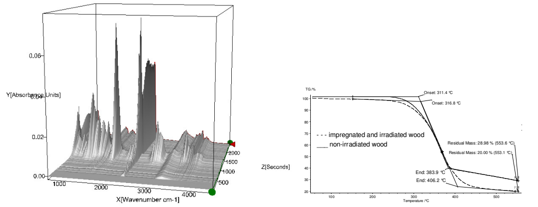


Figure 1: *Vibrational spectra and TGA-IR of wood sample before and after irradiation.*

Conclusions

Vibrational spectra provide information about changes in the molecular structure of different wood type components due to decay, *in situ* polymerization by irradiation. Thermal analysis coupled with structural detectors can provide useful information about natural and composite material composition.

Acknowledgements

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P28

THE USE OF MODEL PROBES FOR ASSESSING IN DEPTH MODIFICATIONS INDUCED DURING THE LASER CLEANING OF MODERN PAINTINGS

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Introduction

Within the conservation practice, concerns have been raised as regards the cleaning of overpaint layers on modern paintings. With the aim to remove acrylics or other related compounds that compose the overpainting, special care should be given to safeguard the original painting, also consisting of acrylic materials.

Experimental

Laser cleaning by a KrF excimer laser at 248 nm (pulse duration 20ns) has been successfully applied in this respect for the cleaning of “The Black Painting” by Ad Reinhardt, in collaboration with the Guggenheim Museum and the Museum of Modern Art of New York (MOMA) [1].

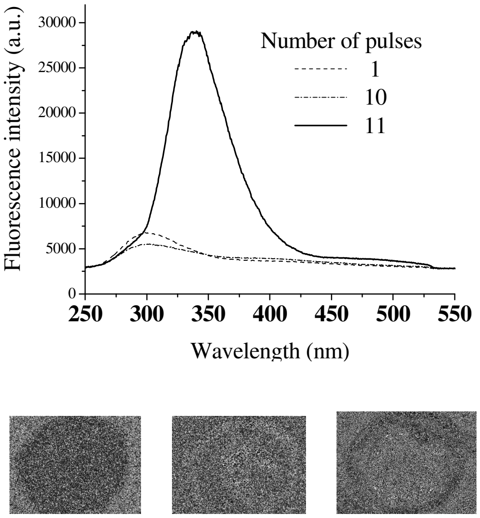
In order to elucidate the extent of any photochemical or structural modifications, induced in the substrate following laser irradiation, a methodology based on the use of a sensitive photochemical and photomechanical model system has been developed [2]. This relies on a probe consisting of a polymeric material (e.g. PMMA) doped with aromatic photosensitisers (e.g. PhenI, NapI) of known photochemistry, coated with uniform layers of acrylics of different thicknesses, and chemical composition (organic and inorganic pigments, such as red alizarin and Prussian blue), simulating real case scenarios.

Results

The laser induced material removal is monitored by the acquired fluorescence spectra of the acrylic paint and the photoproducts created in the polymer substrate via single photon laser induced fluorescence. Once the fluorescence peak of the later is observed, we may conclude that the acrylic layer has been removed and the laser beam affects the substrate.

Conclusions

Practical issues related to the employed laser parameters will be presented and the potential implementation of this methodology for the monitoring of the laser induced mechanisms /processes occurring upon the 248nm cleaning of modern paintings will be discussed.



1st pulse 10th pulse 11th pulse

Figure 1: *Fluorescence spectra of irradiated (248 nm – 4 J/cm^2) acrylic paint casted on 0.5% PhenI/PMMA (350 kDa). The fluorescence peak after the 11th pulse indicates the affection of the polymer substrate, as shown additionally by the optical microscopy observation.*

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P29

DETERMINING OF AGE OF WALL PAINTS – FRESCOS BY MEASURING OF H_2O CONTENTS

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Introduction

We propose a method which is not destructive (in the sense of damaging of the wall paint), and he consists in determining of humidity contents i.e. in measuring of ppm of molecules H_2O. The paint and environment exchange molecules of H_2O and therefore humidity percent changes in time. We shall consider the case when the wall paint remains in the same room. It is obvious that the exchange of H_2O molecules between room and wider environment influences the humidity of the wall paint. The Marcov's graphs will be used [1] in calculations. The cells correspond to the paint, to the room and to wider environment. The fact that the system is closed means that the sum of concentrations will be constant in time.

Basic formulas determining humidity

In the previous section it was said that in the Analysis will be based on closed Marcov’s graphs with three cells [3]. The mentioned graph is given on Fig. 1.

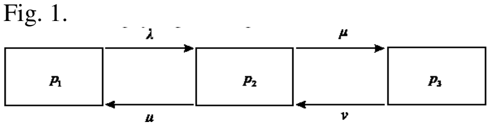

Figure 1: *The closed Marcov’s graph with 3 cells*

On this graph p_1 represents concentration of H_2O molecules in the wall paint, p_2 is concentration of H_2O molecules in the room while p_3 is concentration H_2O molecules in wider environment. The scheme in Fig. 1. shows a system of differential equations determining time dependence of concentrations p_1, p_2 and p_3.:

$$\begin{aligned} \dot{p}_1 &= -\lambda p_1 + \mu p_2 \\ \dot{p}_2 &= -2\mu p_2 + \lambda p_1 + \nu p_3 \qquad (2.1) \\ \dot{p}_3 &= -\nu p_3 + \mu p_2 \end{aligned}$$

The procedure gives the follows system of algebraic equations:

$$\begin{aligned} &(\omega+\lambda)q_1(\omega) - \mu q_2(\omega) = p_1(0) \\ &-\lambda q_1(\omega) + (\omega+2\mu)q_2(\omega) + \nu q_3(\omega) = p_2(0) \quad (2.2) \\ &-\mu q_2(\omega) + (\omega+\nu)q_3(\omega) = p_3(0) \end{aligned}$$

Determining the age of the wall painting

Initial concentrations $p_1(0), p_2(0)$ and $p_3(0)$ are unknown. With help of this sheme we can reproduce paints of investigated wall object and measure its humidity. It could be equal to initial concentration $p_1(0)$. Besides, the age of the paint *T,* which is the main object of our analysis, we must find the distribution frequencies μ, ν and λ, with more diferential equations and numerical methods.

Conclusion

The proposed method of determining the age of wall paint has given satisfactory result: the age *T* can be determined without touch on the paint. This eliminated actually existing effect consisting in influence of walls, furniture and so on to the humidity of room [2]. The main difficulty (shortage) of this approach is the moment of selling the wall paint, since it occurs out of the room included in our theory.

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DEVICING AND APPLICATION OF A PORTABLE LIPS SYSTEM FOR CHARACTERIZATION OF COPPER ALLOYS

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Introduction

Laser Induced Plasma Spectroscopy (LIPS) [1] is a powerful tool for qualitative and quantitative elemental characterization of metal alloys and other materials. The laser ablation of a micro-scale volume (10-100 μm spot size, 0.1-10 μm single pulse-ablation depth), usually does not involve any relevant invasiveness issue for most of the objects. Non-invasiveness along with the potentials for portability and low-cost are attracting a growing interest for this technique. The less expensive typical setup includes an air-cooled passively Q-switched (QS) Nd:YAG and compact spectrometers equipped with CCD array detectors, whereas the most sophisticated and expensive systems are based on electro-optically QS Nd:YAG lasers, Echelle spectrometer, and intensified CCD camera. The unsatisfactory performances of the former and the high cost and the relatively large sizes of the latter, along with the need to achieve an efficient optical collection allowing for easy alignments on the very variable surface shapes of the metal artefacts, led us to design and assemble a novel device (Fig.1), within the project Authentico “Authentication methodologies for metal artefacts based on material composition and manufacturing techniques” [2].

After suitable calibration measurements the apparatus was used for characterising two bronze figurines belonging to the Antiquary Collections of Florence’s National Museum of Archaeology: a satyr and a grotesque subject of uncertain origin, which are stylistically attributable to the Roman Age.

Experimental

The portable device consists of: 1) stable and compact (17 cm head-length) electro-optically QS Nd:YAG laser (1064 nm, 50 mJ/pulse), 2) four compact fibre-coupled spectrometers equipped with CCDs, which cover the spectral range between 200-630 nm with a resolution of 0.06 nm, 3) high numerical aperture optical collector, 4) inspection CCD camera, 5) analysis code.

The quantitative measurements were performed using the method of calibration curves obtained by means of a homemade set of samples and several commercial standards.

The two figurines present evidence of restoration interventions including mild soldering for joining several independent pieces and patination. The main aim was the recognition of genuine fragments and integrated sculptural parts.

Results

Calibration measurements of binary, ternary and quaternary copper alloys (Cu, Sn, Zn, Pb) including depth profile analysis and cross-check comparison with ICP-OES, AAS, SEM-EDX, and TOF-ND were carried out.

A number of analyses were performed on the bronze figurines, which provided a complete compositional picture of all the zones of interest. They allowed distinguishing between authentic fragments and arbitrary integration on the basis of composition, corrosion profiles, and presence of pollutants, such as chlorine and sulphur.

Conclusions

In this work we developed a novel calibrated LIPS apparatus and demonstrated its significant potential in authentication studies. Standalone elemental depth profile analyses can provide real time compositional assays for preliminary authentication screening.

Figure 1: *Experimental setup.*

Acknowledgements

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EDXRF ANALYSIS OF A BAROQUE POLYCHROME WOODEN SCULPTURE

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Introduction

In this work a Baroque polychrome wooden sculpture, portraying the Virgin Mary (fig. 1), was analyzed using Energy Dispersive X-Ray Fluorescence technique.

The scientific examination of artworks has gained increasing interest in the last years, allowing the characterization of materials and techniques employed by the artists, which can be extremely valuable to conservation and restoration treatments. The analysis can also reveal the presence of retouchings (concealed by past restorations), later added areas, changes of design, underpaintings, etc.

X-Ray Fluorescence analysis is a widely used spectroscopic technique in archaeometry to investigate the composition of pigments (in manuscripts, paintings, ceramics and other artifacts), metal alloys, coins and statuary. It is a non-destructive technique that makes possible qualitative and quantitative multielemental analysis with good precision and accuracy.

Experimental

The EDXRF measurements were carried out with a portable system, developed by the Nuclear Instrumentation Laboratory, consisting of an Oxford TF3005 X-ray tube and a Si-PIN XR-100CR detector from Amptek (with 6 mm^2 active area and a 25 µm Be window). The X-ray tube presents a W anode, a 127 µm Be window and maximum operating current and voltage of 0.5 mA and 30 kV, respectively. The angle between the X-ray tube and the detector window is 60°, the source-sample and the detector-sample distances are 4 cm. The system is adapted to a tripod, which makes possible to reach higher regions during the analysis of paintings and statues. In order to identify the pigments used in the sculpture, were obtained several spectra, working at 25 kV and 100 µA, with an acquisition time of 500 seconds and a beam collimation of 2 mm. The spectra were processed and analyzed using the software QXAS-AXIL, from IAEA.

Results

The analytical identification of a pigment involves its colour and composition. Since the chronology of use of most pigments is well documented, is possible to establish the provenance, historical period and, consequently, the authenticity of an artefact. The results revealed the presence of gypsum ($CaSO_4$), used in the preparation layer. In the carnation regions, the artist used vermilion (HgS) and lead white ($2PbCO_3.Pb(OH)_2$). In the dark-brown hairs of the Virgin and angels it was characterized the use of umber pigment ($Fe_2O_3.MnO_2$). In the rosy lips was applied a mixture of vermilion, red ochre (Fe_2O_3) and lead white. In the tunic and in the mantle of the Virgin was identified the use of ochre (red and brown), vermilion, Prussian blue ($Fe_4[Fe(CN)_6]_3.14\text{-}16H_2O$), lead white and a copper based pigment - probably verdigris ($Cu(C_2H_3O_2)_2.2Cu(OH)_2$). In the golden areas were applied gold leaves over the Armenian bole.

Conclusions

The pigments identified in the sculpture, excepting Prussian blue, are used since antiquity and had been reported in several analyses of Baroque sculptures. Prussian blue as pigment was introduced in the beginning of the XVIII century, therefore, the sculpture analyzed in this work seems to be assigned to this period.

***Figure 1.** The analyzed sculpture and the EDXRF portable system.*

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XRF CHARACTERISATION OF THE VARNISHES OF ANCIENT STRINGED INSTRUMENTS

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Introduction

Studies by modern lute-makers assessed that a relationship between quality of sound and timbre of an instrument and the composition of its varnish subsists. Such contribution is so important that, in some cases, is able to compensate possible structural defects of the wood [1]. Thus, the interest in recovering the recipes of the varnish formulated by famous lutists is constantly growing both by artisans and industries focused in the production of high quality instruments. In this work, the collection of stringed instruments of the Conservatorio di Musica "V. Bellini" in Palermo (Italy) has been taken into account to take aim at information about the varnishes composition.

Experimental

Every handicraft instrument has been singled out and catalogued. After the observation in visible and UV lights and having taken pictures, portable milli-XRF measurements were carried out upon two of them: an early 20th century *viola d' amore* from Sicilian School and a finely decorated 18th century cello from Naples School. Details of the experimental parameters are given elsewhere [2].

Results

The XRF spectra of five sampled spots on the *viola d' amore* are reported in Fig. 1. The analysis of these spectra traces back to a faint coloured varnish. Fe peak is referable to an earth (Fe_2O_3) while Pb compounds were often used as siccative for drying oil-based varnish [3]. XRF spectra of the varnish of the cello (not shown) are similar to those relative to the *viola d' amore* except for intensity and the presence of Mn (probably as MnO_2) which enhances the red iron based colour. The XRF spectra of the coloured parts of the decoration present in the rear part of the Naples cello are reported in Fig. 2. Red pigment constists of Hg (probably as cinnabar), black one by carbon black (not detectable by XRF) which, often, was mixed Pb (as lead white) and blue one by Fe (probably as Prussian Blue).

Conclusions

The study permitted to identify the inorganic elements present in the varnishes as pigments for the colouration of the wood and/or additives used to accelerate the desiccation.

Acknowledgements

The authors acknowledge the technical collaboration of Mr. G. Cinà (CRPR), Mr. A. Vitelli (CRPR) and Ms. S. Micciulla during the experimental work. The authors wish to thank the Conservatorio di Musica "V. Bellini" for providing the ancient musical instruments.

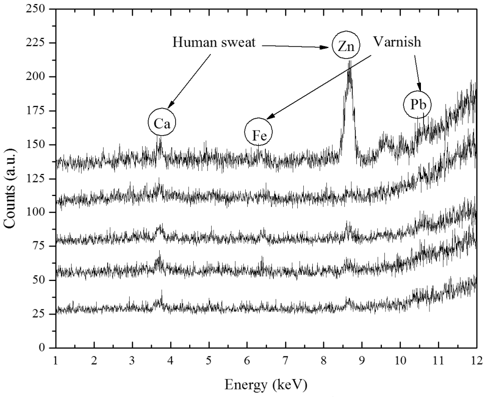

***Figure 1**: XRF spectra of the 20th century viola d' amore from Palermo*

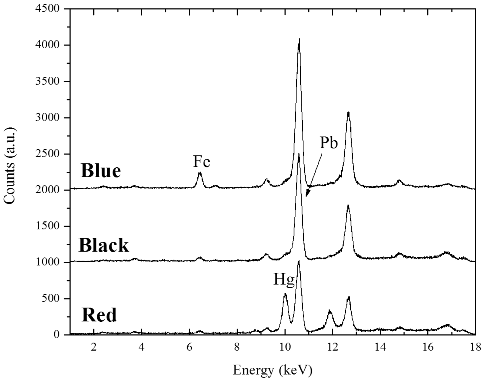

***Figure 2**: XRF spectra of the three-colours decoration of the 18th century cello from Naples*

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PIGMENT CHARACTERIZATION OF 16TH CENTURY JAPANESE NANBAM FOLDING SCREENS

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Introduction

Japanese painting is one of the oldest and most highly refined forms of Japanese art, comprising a wide variety of genre and styles. Its history is a competition between the influence of imported ideas and native Japanese aesthetics, thus making this art form so unique. As paper was introduced in the Japanese Empire around A.D. 610, it quickly leads to the development of art objects made with this rather cheap and transportable new material. During the 16th century, Portuguese traders reached Japan for the first time, initiating active commercial and cultural exchange between Japan and the West, called Nanban Trade. This work is the first study of the materials used to decorate a pair of Japanese folding screens belonging to this period

Experimental

The analysed artworks consisted on a pair of 16th century Japanese folding screens (*Byobu*) signed by Kano Naizen of the Kano school kept practically without restoration interventions. The EDXRF equipment used in this study consists on an X-ray generator from Amptek, the ECLIPSE III with Ag anode (30 kV, 100µA). The detector is an Amptek XR-100CR of Si(Li) thermoelectrically cooled (Peltier effect), with Be window[1]. The components are assembled on an aluminium structure (with 90º geometry) and mounted in a tripod that allows a range of 1.5 m, in order to analyse the screens in all their extent.

Results

The EDXRF analysis and knowledge of the elemental content of the colours present in the print, gave enlightening results regarding the used pigments. The high amount of Hg in the bright red areas implies the use of vermillion (*shu*) while the high amount of Pb the darker red suggested the use of lead red (*entan*). Mercury was also found in brown vestments of the characters. Both green and blue areas presented high levels of Cu, which is consistent with the fact that Malachite (*rokushō*) and Azurite (*gunjō)* were the most used pigments by Japanese artists[2]. Both black and white pigments revealed high content of Ca. Until the 15th century, clay was always used as the white pigment for paintings, but between the 15th and 16th centuries, powdered oyster shell took the place of clay and continued to be used throughout the Edo period until today. Actually, Japan seems to be the only country that used oyster shell as a white pigment, leading us to believe that this was the case of the white pigment in the screens. Concerning the black pigment, no significant high levels of Fe and Mn were found which could be indicative of oxides of iron and manganese. Hence we might suggest the use of a carbon-based black pigment. Historians believed that the panels of these screens were constituted by several layers of paper completely covered with gold leaf over which were applied the pigments. From our study we concluded that this statement was not true, taking into account the absorption by Ca of the incident radiation and the emitted radiation of Au. Au was not used bellow the white and black areas.

Conclusions

The obtained results by EDXRF allowed the establishment of an analysis strategy. The next step is to complete the study with Raman and Optical microscopy analysis.

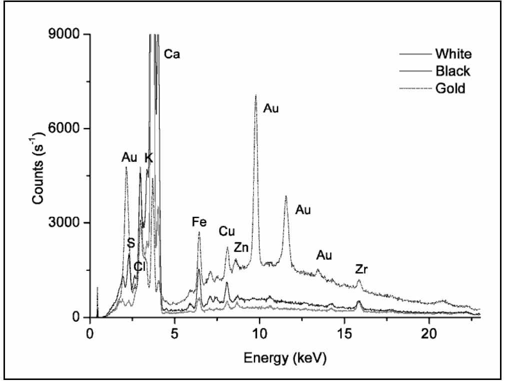

Figure 1: *Comparison of the spectra obtained for the white, black and gold areas. No Au was found in the white and black areas.*

Acknowledgements

Authors would like to thank Dr. Paulo Henriques, Director of Museu Nacional de Arte Antiga, for allowing the study of the Namban folding screens.

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NON-INVASIVE ANALYSIS OF METAL ARTIFACTS FROM THE HISTORICAL MUSEUM OF CRETE: AN APPLICATION OF THE LM^{NT}I LIBS INSTRUMENT

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Introduction

Laser Induced Breakdown Spectroscopy (LIBS) was applied for the examination of a series of Byzantine and Post-Byzantine metal objects from the Historical Museum of Crete in order to identify their qualitative and semi-quantitative composition, information that is essential prior to any conservation treatment. The objects examined were jewellery and small ornaments that could not be sampled. Most of them were identified and registered in the Museum records as lead objects.

Experimental

The analysis was carried out at the INSTAP-SCEC (Pachia Ammos), using LMNT I (el-em-ent-one), a new transportable LIBS instrument that was designed and constructed at IESL-FORTH (Herakleion, Crete) specifically for the needs of non-sampling analysis of ancient artefacts. The main components of LMNTI include: a) compact Q-switched Nd:YAG laser (with power supply), producing 10 ns pulses at 1064 nm with energy up to 50 mJ; b) 0.19 m imaging spectrograph with two diffraction gratings offering spectral resolution of 0.5 nm and 1 nm respectively; c) quartz optical fiber (0.6 mm) for collecting the plume emission into the spectrograph; d) intensified CCD detector and a pulse generating unit to provide proper gating; e) platform on a XYZ translation stage for mounting and positioning objects and samples; f) small color CCD camera for accurate sample viewing and aiming; and g) a personal computer for instrument control and data analysis.

Results

The results of our analysis showed that lead (Pb) is present in very few objects and in a relatively low quantity. Major elements identified include tin (Sn), zinc (Zn), copper (Cu) and silver (Ag). In some of the objects only Zn was detected which appears to be a quite unusual case, while others consist of a Sn-Pb alloy that is very rich in Sn. Variations in the quantitative composition of the alloy that was used for the joins of parts have also been detected.

Conclusions

The compositional analysis of these metal artefacts provided significant information as regards the technology of their manufacture as well as the economical value and consequently the social rank that they represent.

Furthermore, the information obtained was crucial for the choice of the most appropriate materials and methodology to be used for cleaning, stabilization and coating of the objects.

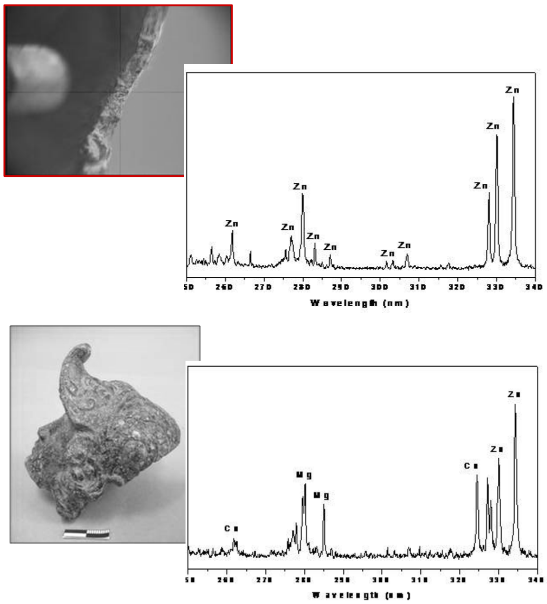

__Figure 1a,b:__ Multiple spot analysis allows the detection of variations between the composition of the core and the surfaces or between various parts of the objects and to adapt the conservation treatment accordignly. I the statuette of Athena the core metal (1a) we detected pure zinc while on the surface (1b) we detected copper on black corrosions spots which suggests that the object may have been copper plated and magnesium that can be attributed to environmental depositions

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ILLUMINATED MANUSCRIPT CHARACTERIZATION BY LABORATORY-MADE PORTABLE XRD AND MICRO-XRD SYSTEMS

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Introduction

The study of illuminated manuscripts has become one of the most important subjects within cultural heritage due to their historical and artistic importance. Previously, sampling was completely necessary for the pigments recognition in these artworks. Nowadays, non-destructive techniques such as micro-Raman and X-ray fluorescence are generally performed [1].

New portable X-ray diffraction (XRD) and micro-diffraction (µ-XRD) equipments have been designed and constructed recently in the C2RMF laboratory; they take advantage of various devices from Synchrotron Radiation. Until now, these systems have been tested for paintings, ceramics, metals, etc., providing information on the crystalline structure of the materials, but they have never been used to study illuminated manuscripts. The main objective of this work is to prove the validity of the new X-ray diffraction systems for this type of works.

Experimental

The two analyzed manuscript are part of the book *Lubab al-Ta'wilfi ma'ani al-tanzil* (L'Alcoran comments) written by Al-Jazin in the XIVth century. The experiments were performed directly on the manuscripts by the laboratory made systems, in reflexion mode by the portable XRD system [2] and in transmission mode by the µ-XRD. In both cases, X-ray tubes with copper anodes were used and the data were collected with imaging plates as 2D detector. The measured area in the different colours (red, brown, yellow, white, black, green and blue) was about 9 mm^2 for the portable system and 1 mm^2 for µ-XRD.

Results

Qualitatively, the results obtained by portable XRD and by µ-XRD are very similar as it is shown in Figure 1. A common observation in all the cases is the presence of calcite, barite and titanium oxide, possibly used in the manufacture of paper and in the preparation layer for the manuscripts. Also, hematite, goethite, cinnabar, brass (Cu-Zn alloy) and litopone were detected in the different colours. No diffraction patterns attributed to crystalline inorganic pigment were found in blue and green colours, due to the presence of organic compounds, responsible for the colour, as already shown by micro-Raman spectroscopy. Increases of the relative intensities in the patterns of the compounds coming from the paper and the preparation layer were observed by µ-XRD. In the case of the experiments performed by portable XRD, higher relative intensities were detected in the patterns, corresponding to pigments because the X-rays do not penetrate to the core of the manuscripts.

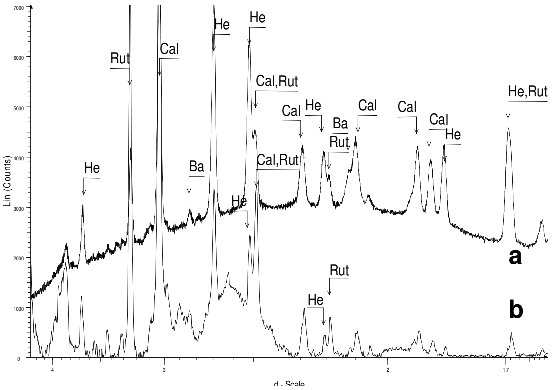

Figure 1: *Comparison of diagrams performed by portable XRD (a) and micro-XRD (b) systems on red colour [He=hematite;Cal=calcite;Rut=rutile;Ba=barite]*

Conclusions

This work shows the validity of the laboratory made non-destructive portable XRD and µ-XRD systems for the study of illuminated manuscripts. The systems provide excellent results although amount of colouring materials is very small. Differences between the results obtained by both techniques due to the acquisition mode are shown.

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EDXRF QUANTITATIVE ANALYSIS OF CHROMOPHORE CHEMICAL ELEMENTS IN CURUNDUM SAMPLES

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Introduction

When dealing with historical jewels, such as crowns, the question about recognizing original parts from substituted ones can be of great importance, also to get information about the history of the jewel itself [1].

Corundum is a crystalline form of aluminum oxide (Al_2O_3) and is one of the rock-forming minerals. When aluminum oxide is pure, the mineral is colorless, but the presence of trace amounts of other elements such as iron, titanium, and chromium in the crystal lattice gives the typical colors (including blue, red, violet, pink, green, yellow, orange, grey, white, colourless, and black) of gemstone varieties. Transparent specimens are used as gems, called ruby if red, while all other colors are called sapphire. It is also possible to grow gem-quality synthetic corundum. The starting point of our work is the possibility to recognize synthetic from natural gems from the study of physic chemical behavior [2]. With this aim we attempted to give a quantitative evaluation of chromophore chemical elements.

Experimental

EDXRF measurements have been performed on different sets of samples of corundum belonging to different rocks of origin (e.g. igneous rocks and metamorphic rocks), and on few synthetic samples product with different methods. We developed an experimental protocol to quantify metallic element content evaluating auto-absorption in the alumina matrix. We exploited both a secondary anode device in order to directly measure transmitted X ray intensity at energies of different chemical elements detected in sapphires samples, and a EDXRF spectrometer to perform quantitative analysis.

Results

Quantitative EDXRF results have been compared with optical absorption spectra, radio-luminescence and photoluminescence analyses. We stress that, even if we deal with trace elements in a light matrix [3], it is not possible to disregard secondary excitation effects.

Conclusions

The preliminary results point out that EDXRF is a powerful tool to give a characterization in terms of chromophore contents and trace elements, for natural and synthetic gems. Conclusions about the range of possible inclusions in corundum gemstones and their correlations with their geological origin can be drown. For instance, while Ti is common both to magmatic and metamorphic sapphires, other inclusions such as Zr or Ca are instead characteristic of the geological environment of gemstones. In fig.1 we report, as an example, the comparison between the spectra acquired from a metamorphic sample from Australia (the red one) and from a metamorphic sample from Madagascar (the blue one). It is evident that elements characterising the provenance sites are present.

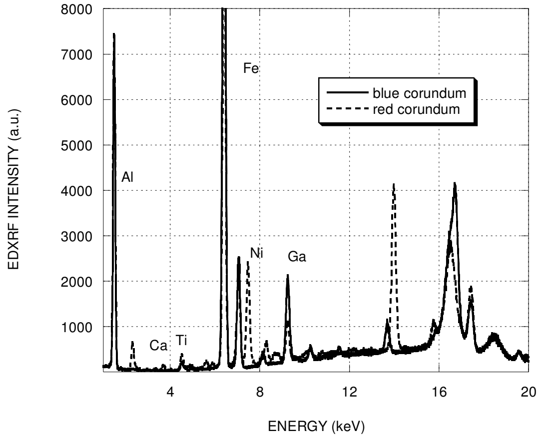

Figure 1: *Comparison between EXRF spectra of two natural corundum samples with different provenance but same geological origin.*

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P37

A NEW PORTABLE LIBS SYSTEM (LMNTII) IN THE ANALYSIS OF CULTURAL HERITAGE OBJECTS

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Introduction

In recent years several research groups have demonstrated that LIBS analysis can be performed using compact equipment and as a result portable LIBS units have emerged that were shown to be useful in the context of environmental analysis or geological surveying [1,2,3]. However, very little work has been reported concerning the analysis of cultural heritage objects by using portable LIBS instrumentation. Following the development of a transportable laboratory LIBS instrument (LMNTI) for the analysis of archaeological objects [4] our laboratory has now developed a new, fully portable LIBS unit (LMNTII) that is presented herein along with selected examples of its use in the analysis of cultural heritage objects.

Experimental

The component selection for the system was based on several factors including size, cost and operational reliability. LMNTII (Fig. 1) is composed of the probe head and the main unit, which fit in a small standard tool case and weigh less than 9 kg. The probe unit includes the laser head, optics to guide, focus and adjust the energy of the laser beam, an optical fibre to collect and guide the plasma plume emission to the spectrograph and a camera for visualizing the object surface and determining the point of analysis. The main unit includes the spectrograph, the power supply of the laser and a timing unit. The laser is a compact, passively Q-switched Nd:YAG laser, emitting 8 ns pulses at 1064nm with maximum pulse energy around ~19 mJ and spot size at the focus around 200 μm. The spectrograph-detector system records the time-integrated emission of the plasma plume covering a wide spectral range, 300 - 640 nm with a spectral resolution of 1 nm.

Results

Initial tests were performed in the laboratory in order to fine-tune operation and define proper measurement parameters. The spectra acquired are characterized by relatively narrow atomic emission lines and low continuum background emission despite the time-integrated emission recording, and this is mainly achieved by maintaining the energy density at relatively low levels ($F< 30$ J/cm^2). Following laboratory tests, LMNTII was used in the context of experimental campaigns in several museums, where various archaeological metal objects were studied. Qualitative analysis is straightforward revealing the major and minor elements in the metal alloy or in the corrosion layers. A semi-quantitative analysis is also feasible, aiding the quick classification of a variety of objects. Furthermore, the system has been used in art conservation laboratories, where pigments in several paintings were analysed.

Conclusions

LMNTII, a portable LIBS instrument, has been developed based on compact and relatively low-cost components and has proven its usefulness and reliability in routine analysis of cultural heritage materials such as archaeological metal alloys and pigments in the museum and conservation laboratory environment.

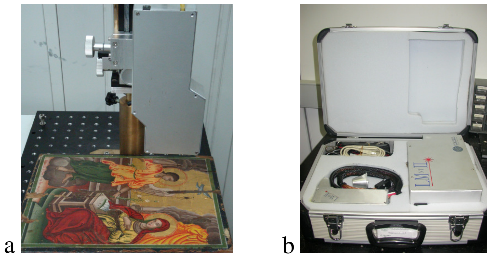

Figure 1: *LMNTII a) analyzing pigments and b) in the carrying case*

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ANALYSIS OF EARLY 20TH CENTURY PIGMENTS IN R. HEINTZ PAINTING USING PORTABLE ANALYSIS SYSTEMS

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Introduction

The "Centre Européen d'Archéométrie" from the University of Liège favours the non-destructive techniques allowing direct analysis on art objects without any sampling or sample preparation. The composition of the pigments is a source of valuable information such as decisive clues on the origin of the painting by change of the composition of the pigments through history. These analyses can also provide information on the state of conservation of the painting and pigments degradations. This work will present physico-chemical analysis of pigments used by Richard Heintz, a 20th century landscape Belgian painter (Fig. 1). Four paintings and several colour tubes from R. Heintz were analysed by using different non-invasive techniques (EDXRF, UV-VIS-NIR, Raman spectroscopy) and pigments were identified as well as the possible anachronisms which follow from these analysis. A portable EDXRF coupled with UV/Visible spectroscopy system was developed and used for this fieldwork analysis in close collaboration with a portable micro-Raman system from the University of Ghent.

Experimental

The transportable system for EDXRF used was designed and realised at the IPNAS laboratory [1]. We used a traditional EDXRF configuration coupled with a StellarNet UV, visible and near infrared spectrometer. The XRF data acquisition has been made through a home made electronic MCA. The reflectance spectra and the colour parameters are subsequently obtained by software. The core of the mobile art analyser (MArtA) for Raman analysis is a portable Raman imaging microscope (PRIM, Spectracode, West Lafayette, IN, United States) [2].

Results

Characterization of the palette has been achieved by the above-mentioned methods and some variations in the materials have been found such as for yellow and white pigments. For example yellow pigments mainly contain subsequently iron oxides, chromium and zinc and barium in different paintings. Other pigments are recurrent in Heintz's work such as chromium green, cobalt and Prussian blue.

Conclusions

According to our results, it seems that Heintz's palette has changed little throughout his career. Despite tones visually different, the four analyzed paintings have in common most of analyzed pigments. Moreover regarding Heintz's colour tubes analysis, anachronisms has been found out.

Figure 1: *R. Heintz painting: "La roche noire au soleil de mars", 1916, Musée de l'Art wallon de la ville de Liège, inv. 499.*

Acknowledgements

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RADIOISOTOPE VS. MINI-X TUBE EXCITATION IN AN AMPTEK X-123 PORTABLE XRF SPECTROMETER: A COMPARATIVE STUDY

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Introduction

A small compact portable XRF spectrometer based on an Amptek XR-100CR Si-PIN detector using 3 excitation heads containing ^{55}Fe, ^{109}Cd and ^{241}Am radioisotope for excitation has been previously developed for *in situ* analysis of art and archaeological objects [1]. Due to administrative difficulties of the transportation and entering to the museums and galleries, and some aversions to the use of radioactive materials as well, no real “breakthrough” in true *in situ* analysis has been achieved. The recent advent of the small and lightweight but powerful Mini-X X-ray tube from Amptek, however, offers an alternative to the radioisotope excitation in this “mini size scale”, too. In addition, the new giant matchbox sized Amptek X-123 spectrometer integrating the Si-PIN detector, the preamplifier, the pulse processor and an MCA has allowed even more miniaturisation. This presentation reports the results of comparisons of the capabilities

Experimental

The Amptek X-123 X-ray spectrometer connected to a notebook was either equipped with the excitation heads containing ^{55}Fe and ^{109}Cd, or the Amptek Mini-X X-ray tube with Ag anode was used to produce the X-ray fluorescence lines. The excitation and detection geometries were chosen to be as similar as possible.

Results

Systematic measurements were made on different MicroMatter standard foils using different tube parameters and filters. X-ray spectra on the the same spot of a painting were also taken. Sensitivity curves and detection limits were determined. The effective analysed areas were also determined using different collimations. X-ray dose maps around the two different irradiation configurations were also measured. An illustrative example is given on Fig. 1, where X-ray spectra of a one euro coin taken with the two different excitation configurations are displayed. Taking into account the actual age of the radioactive source the characteristic X-ray intensities in the spectra are roughly the same.

Conclusions

The Mini X X-ray tube mode of excitation provides significantly shorter accumulated measuring times even in a rather conservative low current operating mode providing the same sensitivities. The absence of any radioactive materials, on the other hand, makes it the dissemination of the *in situ* use of XRF for non-destructive analysis in museums, art galleries or even in excavations easier.

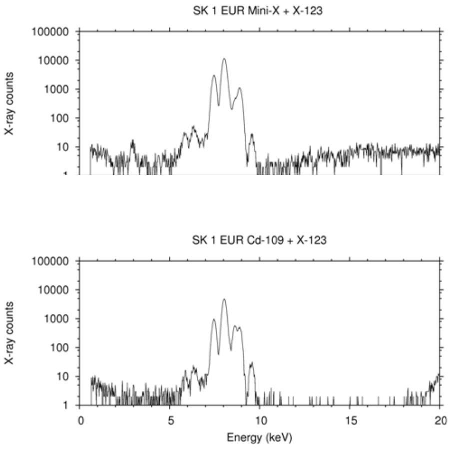

Figure 1: *XRF spectrum of a 1 euro coin taken with Amptek Mini-X tube excitation using 40 kV high voltage and 1 μA current (upper curve), and by the use of a* ^{109}*Cd ring source of 370 MBq nominal activity (lower curve).*

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MARAJOARA CERAMICS ANALYSIS BY EDXRF AND MULTIVARIATE STATISTICAL

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Introduction

In this work 102 fragments of Marajoara pottery pubic covers, belonging to the National Museum collection, were analyzed using EDXRF and Multivariate Statistical Analysis in order to identify possible groups of samples that present similar behaviors or different characteristics. Marajoara ceramics (Marajó Island, Brazil) represent one of the most beautiful and sophisticated styles of the pre-Columbian art and its decorative techniques show intricate geometric designs, representing a mythology based on the local fauna. The period of major growth of this culture occurred between the V and XIV centuries and its disappearance during the first decades of the European domination, as a result of wars and missionization [1]. The pottery pubic covers could be either red slipped and polished or white slipped and covered with geometric red or red/black designs, and were anatomically adjustable to the body, containing holes on its corners for string attachment.

Experimental

EDXRF measurements were carried out with a portable system, consisting of an X-ray tube Oxford TF3005 with W anode, operating at 25 kV and 100 µA, and a Si-PIN XR-100CR detector from Amptek. Details on the experimental EDXRF portable system are given in ref. [2]. In each one of the fragments were analyzed 6 points (3 in the front part and 3 in the reverse) with an acquisition time of 600 s and a beam collimation of 2 mm. The spectra were processed and analyzed using the software QXAS - AXIL (IAEA). Multivariate Statistical Analysis (PCA) was applied to the results.

Results

The 102 fragments showed the same elements and similar XRF spectra. The elements identified in the samples were: K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Ga, Se, Rb, Sr, Y, Zr and Pb (Fig. 1).

In this work, PCA was performed using the average counts for each of the sides of the fragments. The results revealed a clear cluster separation to the samples in two distinct groups (Fig. 2).

Conclusions

This result suggests that some samples proceed from distinct localities, showing small differences in the chemical composition of the original clay from which they were produced. This information will give an important aid to a more accurate classification of these artefacts.

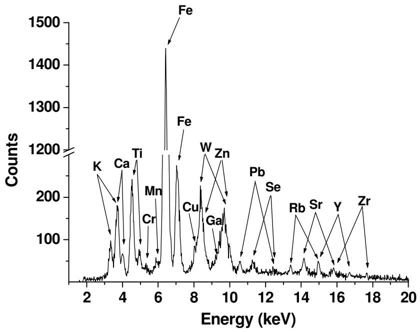

Figure 1: *Characteristic XRF spectrum of the pubic cover.*

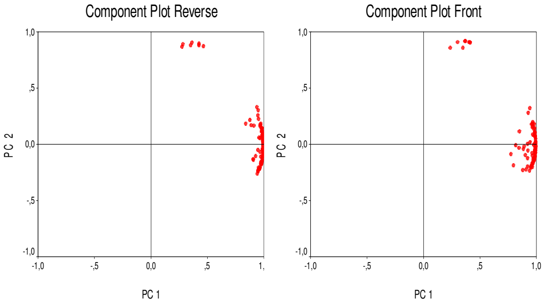

Figure 2: *Score plot of the reverse and of the front part of the samples*

Acknowledgements

This work was funded by Brazilian Agencies CNPq and FAPERJ.

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X-RAY SPECTROMETRY INVESTIGATION OF TWO RAPHAEL'S PAINTINGS

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Introduction

We developed an integrated experimental system for multispectral analysis and X-ray tomography and applied it to the study of two Raphael's paintings, namely the very recently restored by Opificio delle Pietre Dure "*Madonna del cardellino*" of Uffizi Galleries in Florence and the "*St. Martin with a Poor Man*" of Amedeo Lia Museum in La Spezia, Italy, aiming to investigate the execution techniques, the composition of used pigments and the conservation status of a few works by such a great artist of Italian Renaissance. Moreover, these analyses are useful to test and verify the usefulness of the advanced tools here proposed for studies of paintings and frescoes.

Experimental

It is well known that Compton scattered radiation, produced by unpolarized incident photons, has a circular symmetry around the direction of the incident beam. This property means that the Compton cross-section does not change along the circular path determined by the rotation of the plane defined by the direction of incident photons and the scattering angle, θ. This characteristic was then used to develop an experimental assembly with axial symmetry [1] where both the source and the detector were positioned on the same axis in an essential backscattering configuration (mean scattering angle $\theta \approx 160$ degrees). The range of scattering angles, $\Delta\theta$, determines an annular profile for the detector collimator and, as a consequence, all the photons having a scattering angle within $\Delta\theta$ may be detected. The axial invariance of the Compton cross-section, together with the large area of the detector collimator, strongly enhances the number of detected photons.

The basic ECOSP apparatus therefore consists of a light NaI detector with a computer assisted acquisition posed on an xyz movement slit whose configuration depends on the in situ environment [2]. The sensitive volume is approximated by a cylinder – 3 mm diameter - entering the sample for its entire depth. The annular shape of the detector collimation is a consequence of the source head position and a further circular shield which may produce a shadowing of the neighbouring layers. The ECOSP apparatus has been used in the analysis of *Madonna del cardellino*, representing a more powerful and extensive tool than traditional XRF spectrometers.

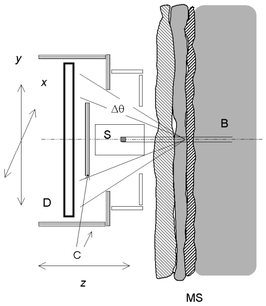

Figure 1: *Planar sketch (not in scale) of the ECOSP apparatus at work on a mural structure (MS). S, shielded source head; B, incident beam; C, collimator rings: D, detector; x, y and z are the spatial coordinates.*

Results

Our analyses confirm the results of previous and independent similar investigations of other Raphael's works and, above all, they allow us to perform X'ray spectrometry measurements on the whole paintings and not only in selected points or regions and finally put new evidence on the autography of Amedeo Lia *St. Martin with a Poor Man* as supported by former attributions due to Carlo Volpe and Federico Zeri.

Conclusions

The examination of few important paintings shows that the present technique is suitable for applications to the cultural heritage and particularly for inspection of frescoes and underlying mural structure because of the peculiar backscattering experimental configuration.

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APPLICATION OF PORTABLE (HANDHELD) NITON XRF ANALYSER IN SOME ARCHAEOMETRY PROJECTS

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Introduction

Our research group has recently invested in a portable and handheld XRF instrument (NITON XL3t 900) as a part of a long term tender in field of archaeometry. This technique is a very novel one in this field of interest in our country and there is a great demand for it. First of all we plan to map the possibilities of this portable instrument, studying the effect of parameters on quantifying such as samle type (metal, alloy, ceramic, glass), sample geometry (especially the surface curvature), matrix effects. During this studies we have measured reference materials (soil and rock), then many artefacts such as terra sigillata samples, ancient alloys (gepida clasps, roman fibules, coins) and some type of glazes. Comparison will be made between our results and that of measured conventionally (non portable XRF).

Experimental

The portable XRF analyser is an energy dispersive NITON XL3t 900 model from Thermo Scientific, equipped with an 50 kV x-ray tube (Ag anode) and a Si PIN detector [1]. Measuring spot size is about 10 mm. According to the saple type data acquisition time (measuring time) is 30-120 secundum. Light elements (Mg, Al, Si, P, S, Cl, K, Ca, Ti) can also be measured with help of He-purging system which is easily attachable to the instrument. Gepida and roman artefacts was provided by Xantus János Museum of Győr, terra sigillata samples and certificated reference materials (NCS DC and GBW:soil and rock) were from Institute for Geochemical Research Hungary.

Results

Although we are at the beginning of applying this XRF analyser, many excellent features can be seen even now. Most advantage one is that there is no need of sampling and destruction of the given sample and reliable qualiytative and quantitative data can be given in rapid measurements. Best results are in case of samples with even, non bended surface where the gap is minimal between the sample and the detector and they are purpendicular to each other. Data obtained from measuring of standard material by XRF are in good accordance with certified values. In case of terra sigillata artefacts with strongly bended surface there are some great deviations in data obtained by conventional and portable XRF method so this geometrical problem must be solved. In case of measuring ancient (3-5. century A.C.) gepida alloys from diffrent burial places and tombs form Hungary it turned out not to be made of bronze as it is believed by today but a kind of brass. There was no any trace of tin but more than 10 percent zinc besides copper in all cases. These results can force to revise some theories about alloy making in a given historical period.

Conclusion

Portable NITON XRF analyser can be used very effeciently especially with portable He-purging system (for measuring so called light elements) for measuring archeological samples of many kind (alloys, ceramics, glasses, glazes). The instrument (ca. 1,5 kg) can be carried easily to anywhere so there are great possibilities to collect important data even from the most valued samples which are not transportable.

Acknowledgements

This work is supported by The Hungarian Scientific Research Fund (OTKA) (PD 75740).

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ELEMENTAL ANALYSIS OF LEAD SEALS OF XII-XVIII CENTURIES BY X-RAY FLUORESCENCE

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Introduction

Seals have been used for the authentication of documents since ancient times. Although the way of corrosion progresses had been proposed and studied [1,2] the conditions that cause its variation are far from being completely understood. In the present work we analyzed more than 50 lead seals showing different states of corrosion, some of them from the same provenance and period of time. The elemental composition of lead seals has been neglected and its influence for preservation totally ignored. The influence of their chemical composition must play an important role in the process, along with the storage conditions. This work aims to establish a relationship between the data collected through a non-destructive analytical method (EDXRF), using different equipments and software.

Experimental

The analysed samples include lead seals from the XII to XVI centuries. The portable spectrometer is an Amptek´s ECLIPSE III (30 kV, 50μA) X-ray generator (no additional cooling unit necessary) with a silver anode and an Amptek´s XR-100CR Si(Li) detector, thermoelectrically cooled (Peltier effect). The detector has a 7 mm^2 area and a beryllium window 12.5 μm thick. The beam is collimated through a tantalum pinhole. The acquisitions were obtained through Amptek software PMCA. The spectra analyses were performed by WinQXAS.

Another spectrometer used has an Ortec detector, High Purity Germanium (HPGe) p-type, with a POP-TOP cryostat (with a cooling system). The detector has an 80 mm^2 area, a beryllium window 12.7 μm thick and a Ge thickness of 7 mm. The radiation sources used were ^{55}Fe (5.9 keV) and ^{241}Am (59.5 keV).

Results

The constituent elements of the lead seals are the same in all the analysed samples. However there is a variation in their relative concentration. Using a higher energy source, important differences in the relative concentrations of tin (Sn) and antimony (Sb) have been found. The presence of these elements seems to help the slowing down of the lead oxidizing process.

Conclusions

The pitting corrosion (started by the attack of organic volatile acids) [1] and general corrosion are evident in many lead seals. The whitish corrosion products are mainly lead carbonates [3]. Seals with the same age and different states of corrosion have been analysed. Lead is a very dense metal which makes the study by non-destructive analysis difficult. Therefore it is not surprising that the identified elements are the same. A larger amount of tin (Sn) in the lead matrix induces a higher resistance to corrosion, although it does not stop it. However, a smaller amount of tin (Sn) does not always correlate with a poor conservation state. The environmental and storage conditions play an important role in this process. Further studies are being conducted to obtain more data in order to better protect this kind of collection.

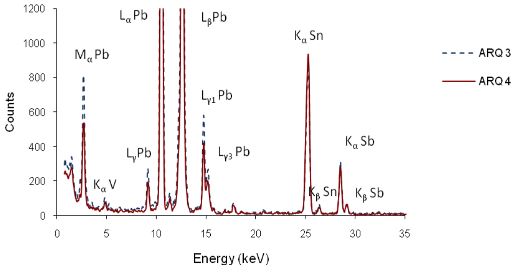

Figure 1: *X-ray fluorescence spectra of lead seals from the XV century, (with a ^{241}Am source).*

Acknowledgements

This work was funded by the FCT ("Corrosion causes and conservation methodologies of lead seals appended from parchments from the Archive of the University of Coimbra"- PTDC/HAH/73753/2006). We acknowledge the Director of the Archive of the University of Coimbra for all the support.

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TRANSPORTABLE SYSTEM FOR MICRO X-RAY FLUORESCENCE SCANNING OF HISTORICAL MONUMENTS

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Introduction

X-ray fluorescence (XRF) analysis plays an important role in investigation of art and archaeological objects. Since these objects could be very heterogeneous, classical XRF analysis provides information on their composition that is averaged over relative large of the surface. Otherwise, the microanalysis determines the presence and concentrations of chemical elements in a given spot, but this place may not be representative and the results of analyses can lead to incorrect interpretations. The best solution, even time consuming, is then the scanning of the chosen part of object surface. For this reason, the micro X-ray fluorescence spectrometer was designed and constructed at the Czech Technical University in Prague.

Experimental

The spectrometer enables spot analysis, line scan as well as mapping with a step of up to 10 µm. The whole system consists of 3 parts. The first part is the X-ray source which contains an X-ray tube (max. 50 kV and 1 mA) with polycapillary focusing X-ray optics (provided by X-Ray Optical Systems, Inc.). The beam size is about 20 µm at the working distance of 5 mm. X-rays are detected with the Amptek spectrometer X-123 consisting of the thermoelectrically cooled Si-PiN detector and the integrated evaluation electronics. The third part is the positioning system consisting of engines, rods, and fixtures (Fig. 1). The detector and the source are usually stable and the samples are fixed to the positioning system. On the other hand, measurements of big objects require movement with the source and the detector, while the artefact is immovable. Data acquisition and the operation of motors are synchronized. In-situ analysis is possible because all parts of the XRF system are easily transportable and the device is positioned on a pedestal to reducing vibration during measurements.

Results

The micro X-ray fluorescence spectrometer is applied to such surveys, when the fine structures of antiquities have to be recognized. Tests were performed with pieces of pottery, corroded metals, and paintings, inks, and pigments used in illuminated manuscript were studied too.

Conclusions

The scanning XRF microanalysis is valuable technique. Since the mapping is time consuming process, the most of artefacts are quickly analyzed with traditional XRF and if the result is indistinct, spot analysis or scanning with micro XRF system is then applied.

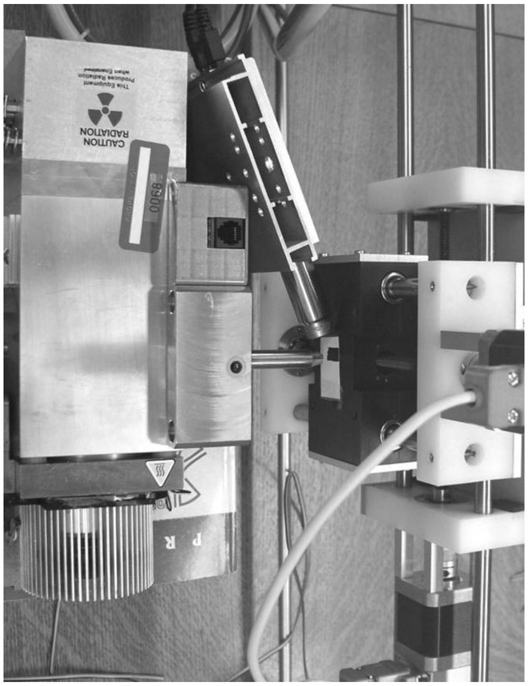

Figure 1: *Photo of the device for scanning micro XRF analysis. X-ray source is on the left, positioning system on the right, and the detector is rather at the top.*

Acknowledgements

This work was performed within project MSM6840770040 of the Ministry of Education, Youth and Sports.

X-RAY FLUORESCENCE ANALYSIS OF THE SILVER ALTAR IN THE OLD BRNO BASILICA OF THE ASSUMPTION OF OUR LADY AT MENDEL PLACE

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Introduction

The Basilica of the Assumption of Our Lady is a true jewel amongst Gothic architecture in Moravia. The widow Queen, Eliška Rejčka, established the Cistercian convent in 1323 next to the old parish church of Our Lady. This became known as Aula Sanctae Mariae, or the Queen's Convent. In 1782 the Augustinian monks moved here from their original site next to the church of St. Thomas, which is today on Moravian Square.

Figure 1: *The Silver Altar in the Old Brno Basilica of the Assumption of Our Lady*

The Order of Augustine of Brno sought permission from the Holy See in 1727 to save coins in honor of the icon. Permission was granted May 5, 1736, and the prior had already signed an agreement with the goldsmith Johann Georg Herkommer, an Augsburg goldsmith, for building an altar to host the icon. This is how the "Silver Altar" came to be, along with its matching silver candelabra, service of three silver chalices, silver pitchers, and trays, monstrance's, and Bishop's crook. Vestments were included too.

Experimental

Within the first step of the restoration of the Silver Altar, some parts of the decoration were dismounted and analyzed with X-ray fluorescence (XRF) method. Short measurements with a small X-ray tube (Oxford Instruments, max. 30 kV and 0.1 mA) and a portable Amptek Si-PiN detector enabled quick characterization of used materials and recognition of gilding. The diameter of the X-ray beam was approximately 500 μm.

Figure 2: *X-ray fluorescence analysis of the gilded secession decoration of the Silver Altar*

Results

The analyses proved that original decoration components, especially the statues, are silver. The younger decorations of the Silver Altar are made of wide scale of materials, particularly bronze, brass, and alpaca that were gilded in some cases.

Conclusions

Some decoration components of the Silver Altar were analyzed non-destructively with XRF technique. The results of the analyses stand conservators and historians in good stead.

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SCREENING AND ANALYSIS OF ARCHAEOLOGICAL SOILS BY LIBS

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Introduction

Laser induced breakdown spectroscopy (LIBS) is a spectrochemical technique appropriate for the analysis of a wide variety of materials and as such has been investigated in recent years regarding its potential in archaeological science, in particular as a tool, which can offer survey capabilities in the context of field applications. [1,2] In this work we present recent results from our investigation on the use of LIBS for screening and analysis of archaeological soils. The elemental composition of soil in and around archaeological or historical sites might be correlated with the nature and distribution of various activities across that site, for instance, metallurgical, agricultural, animal raising, on the basis of specific elemental markers. [3,4]

Experimental

A standard laboratory LIBS setup was used, consisting of a nanosecond pulsed Nd:YAG laser (operating at 1064 or 355 nm), an intensified-CCD detector couple to a high resolution spectrograph (Mechelle 5000, Andor Technology) and appropriate optics. In the LIBS experiment, the laser was focused on the sample surface (energy density ~70 J/cm^2), leading to formation of plasma. The light emitted by the plasma was collected with an optical fiber, transferred into the spectrograph, where it was spectrally resolved and then it was recorded on the ICCD detector. A series of model samples based on clay and alumina matrices, spiked with various metals at concentrations in the hundreds of ppm range were examined along with selected real samples. All soil samples were pressed in the form of pellets for the LIBS analysis.

Results

LIBS spectra obtained from a standard soil sample (Soil #7) show strong emission lines from all major elements (Si, Ca, Al, Fe, K, Mg, Ti and Na) while certain minor elements such as Mn (630 ppm), Sr (108 ppm), Rb (50 ppm) and Ba can be detected unambiguously. On the other hand, most of the elements present at concentrations below 100 ppm were not detected and possibly require further optimization of measurement conditions. This prompted a series of measurement with model samples composed of clay or alumina spiked with metals at concentrations in the range of 100 to 1000 ppm. Using the clay samples, analytical emission lines were determined for most metals including Ag, Au, Sn, Ti, Mn, Ba, Sr, Cr, V, Pb, Co, Ni, Zr and Rb. In addition, calibration curves were obtained from selected metals (Ag, Au, Hg, Cu) in alumina matrix that can be used for the quantitative determination of these elements by LIBS.

Conclusions

The LIBS technique can be a useful tool for archaeological soil analysis, in particular if this can be done in the filed with the use of a mobile instrument. Our results show that screening of soils can be quite straightforward but this capability can be further enhanced by using chemometrics techniques. On the other hand further optimization is needed for obtaining sensitive and reliable determination of trace elements.

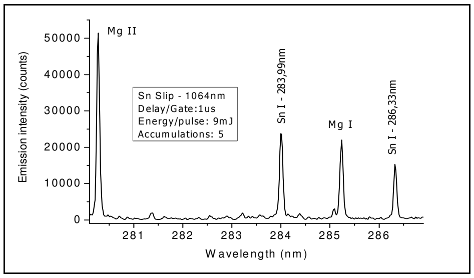

Figure 1: *LIBS spectrum of model clay sample spiked with Sn at 1000 ppm. Prominent emission lines from Sn are shown. (*λ_{LASER} *: 1064 nm).*

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NEAR-FTIR SPECTROSCOPY FOR THE NON-INVASIVE IDENTIFICATION OF NATURAL POLYMERS IN EASEL PAINTINGS

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Introduction

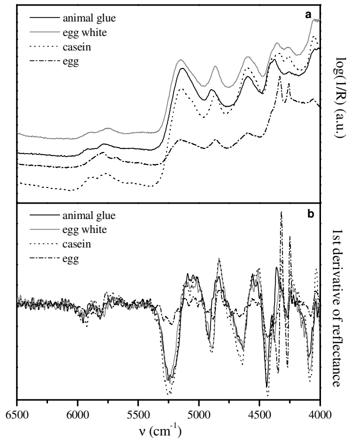
In order to obtain information about organic materials used in easel paintings trough a non-invasive approach we have exploited near infrared spectroscopy which has been only sporadically used in the field of cultural heritage [1,2,3]. In this work an initial database, containing non-invasive near-FTIR spectra of the most used substances in art objects e.g. binders, varnishes and some pigments, was obtained. To highlight the significant differences inside each group of binders as lipid, proteinaceous, natural gums and varnishes, first derivative mathematical function were applied to the spectra. Afterwards laboratory model samples simulating easel paintings were prepared and reflectance near IR spectra were collected. First derivative was applied to verify if it's possible to point out the presence of more components than those identified on the spectral data. An easel paint case study is used to check the potential of the first derivative spectra to analyze the present organic compounds in the paint in comparison with the GC-MS analysis.

Experimental

Reflectance FT-IR spectra were recorded using a compact portable JASCO VIR 9600 spectrophotometer equipped with a near-infrared fiber optic sampling probe. The optical bench is made up of a halogen lamp as source, a Michelson interferometer equipped with a CaF_2 beam splitter and room temperature InGaAs detector. The system weighs about 35 kg and its dimensions are 50x50x50 cm^3. The spectrophotometer is equipped with a silica-glass fiber optics Y sampling probe. The spectral range is 12500 to 4000 cm^{-1} and the resolution is 4 cm^{-1}. Spectra Manager software from Jasco with Savitzky-Golay algorithm was used for the first derivative. Painting materials (binders, varnishes and pigments) have been applied on a glass slides and three spectra for each one were collected to construct the database. Pictorial models were prepared using wood supports to reproduce easel painting. The wood supports were coated with a gypsum ground in animal glue. Single layers of the different pigments were spread on the supports using protein and lipid binders in a pigment/binder ratio suitable to obtain a workable paint. Some ones of these were covered by a final layer of natural varnishes.

Results

As an example of the study in Figure 1a near-FTIR spectra of proteinaceous binders are compared. The characteristic signals for proteins are the combination bands of amide II and the first overtone of carbonyl stretching at about 4600 cm^{-1} and stretching and bending of NH which occurs at 4880 cm^{-1}. Egg can be easily recognized due the methylenic C-H combination bands and their overtones mode related to the lipid content. The derivative forms of proteinaceous spectra (figure 1b) show several differences in the range 6500 - 4000 cm^{-1} both in the shape and in the frequencies and intensity ratios of the bands. Therefore by first derivative it is possible to distinguish undoubtedly an animal glue from a casein or egg white and vice versa.



The portable near-FTIR spectrometer has been successfully exploited to study of an eighteen century easel painting, allowing for the non-invasive identification of terpernic resin and animal glue as confirmed by GC-MS analysis selected on micro-samples.

Conclusions

In this work we have exploited near-FTIR spectroscopy for the identification of natural polymers in easel paintings. The low molar absorptivity of NIR bands allows to work in reflectance mode without encountering problems of spectral distortions, while the drawback of a poor specificity and matrix effects can be partially overcome using first derivative mathematical function.

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X-RAY FLUORESCENCE ANALYSIS OF THE ANJOU BIBLE

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Introduction

The Anjou Bible is a unique bible manuscript originating from the beginning of the fourteenth century at the court of Robert I of Anjou, king of Naples.

The illuminated bible circulated among royals until the beginning of the sixteenth century. At that time, via the Bishop of Arras, the manuscript ended up at the library of the Arras College in Leuven (Belgium) and since 1970, the manuscript is deposited at the Maurits Sabbe Library of the Theology Faculty of the K.U.Leuven.

The bible contains 338 folios with two full-page miniatures and more than 160 decorated initial and marginal illuminations. Despite the fame and the richness of the manuscript, it has almost never been reproduced or displayed in public.

In May 2008, a conservation and preservation project started offering the possibility to examine the manuscript in the laboratory.

Experimental

The XRF measurements are carried out using an ArtTAX® µXRF spectrometer (Bruker AXS Microanalysis, Germany) equipped with a Rhodium X-ray tube (50kV, 500µA, 50 keV, Mo25µm filter, in air, 120s) [1]

Results

XRF measurements carried out on the opening miniature of the diptych representing Robert I of Anjou enthroned, reveal a very rich pallet. Mineral pigments are combined with organic colorants.

For the red colors vermilion, red lead, red earth pigments and organic reds are present in different color intensities.

Azurite and probably lapis lazuli are used for the blues while the green areas show the presence of cupper green, possibly in combination with lead tin yellow.

The use of gold, silver and tin, either as foil or as "paint" raises the splendour of the miniature executed by the Napolitanian illuminator Christophorus di Orimina .

Conclusion

Although having a long history, the Anjou Bible was now for the first time ever examined in detail.

The combination of highly detailed photographs with transmitted light in combination with the non destructive XRF analysis not only provides more insight into the craftsmanship of the miniaturist but is also needed to make correct decisions during the conservation restoration project.

Acknowledgement

The project is funded by the InBev-Baillet Latour Foundation.

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APPLING PYROLYSIS – GAS CHROMATOGRAPHY/MASS SPECTROMETRY TO THE IDENTIFICATION OF ORIENTAL LACQUERS: STUDY OF TWO LACQUERED SHIELDS

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Introduction

Oriental lacquers are natural polymers obtained from three species growing in different regions of Asia: *Rhus vernicifera* (China, Japan and Korea); *Rhus succedanea* (Vietnam and Taiwan); and *Melanorrhoea usitate* (Myanmar and Thailand). Lacquers have been used as coating materials for thousands of years in objects made of wood, ceramic, leather and metal [1, 2].

Lacquers polymerize through an enzyme-catalyzed oxidation mechanism leading to the formation of films with a high level of cross-linking, that are insoluble by most solvents and difficult to analyse by traditional wet chemistry methods [2]. Analytical pyrolysis (Py-GC/MS) was successfully applied to the characterization of these films, allowing to distinguish the three types of lacquer [2, 3]. The identification of lacquer films is important for conservation and restoration purposes, as well as for art history studies because it allows the determination of lacquered objects origin.

In this work, two lacquered shields imported from Asia were studied by Py-GC/MS and FTIR, to assess the identification and origin of the lacquer. Details of the lacquering technique are also reported.

Experimental

Samples from the shields were collected and studied by FTIR and Py-GC/MS. Cross-sections of the samples were prepared and examined using a Leitz WETZLAR optical microscope. Reference lacquer films from Japan, Vietnam and Myanmar were prepared and analysed by Py-GC/MS. Py-GC/MS experiments were carried out with a CDS Pyroprobe 2000 heated filament pyrolyser, attached to an Agilent 6890N gas chromatographer equipped with a 5975N mass spectrometer. FTIR spectra were obtained in a Thermo Nicolet Nexus 670 FTIR spectrometer coupled to a Continuμm IR microscope.

Results

The Py-GC/MS analysis of reference lacquer films show that the three kinds of oriental lacquers have distinct mass chromatograms profiles (Fig. 1) for the ions m/z = 104 (alkenylbenzenes) and m/z = 108 (alkylphenols).

The mass chromatogram profiles of the lacquer from the shields were compared with that of references, and it was found that one shield was lacquered with *R. succedanea* lacquer whereas the other with *M. usitate* lacquer.

Cross-sections from the two shields are different, and FTIR analysis revealed that both shields have ground layers made of different materials.

Conclusions

Py-GC/MS is an efficient and versatile technique to identify oriental lacquers. The two shields have different geographical origins, and the techniques employed in their execution are also different.

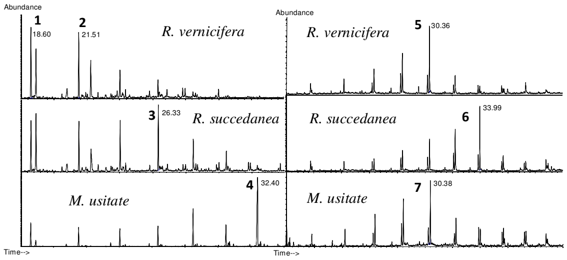

Figure 1: *Mass chromatogram profiles for the ions m/z=104 (left) and m/z=108 (right) of the three types of lacquer*

Acknowledgements

This project was supported by Fundação para a Ciência e Tecnologia (PhD grant SFRH/BD/27573/2006). The authors wish to thank Prof. Miyakoshi (Meiji University) for the lacquer references.

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STUDY OF A NAMBAN PAIR OF STIRRUPS: PY-GC/MS POTENTIAL TO DISTINGUISH ORIGINAL FROM RESTORATION

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Introduction

Namban style has emerged from the early contacts between Portuguese and Japanese cultures in the 16th century. Namban lacquerware was made with Japanese materials and techniques, following European influences and demands. On the other hand, a group of Namban objects displaying Portuguese figures, probably made exclusively for the Japanese market, has appeared [1].

Oriental lacquers are natural polymers obtained from three species growing in different regions of Asia: *Rhus vernicifera* (China, Japan and Korea); *Rhus succedanea* (Vietnam and Taiwan); and *Melanorrhoea usitate* (Myanmar and Thailand) [2, 3]. Lacquers polymerize through an enzyme-catalyzed oxidation mechanism leading to the formation of highly cross-linked films difficult to analyse [2]. Analytical pyrolysis (Py-GC/MS) was applied to their characterization, allowing distinguishing the three lacquer types [2, 4].

In this work, Py-GC/MS was successfully applied to discriminate original from restoration layers of a Namban pair of stirrups. The lacquering technique was studied using Py-GC/MS and Fourier Transform Infrared micro-spectroscopy (FTIR-µs). The influence of pigments in the identification of lacquer is also discussed.

Experimental

Red lacquer samples from the stirrups were collected and studied by FTIR and Py-GC/MS. Cross-sections of the samples were prepared and examined using a Leitz WETZLAR optical microscope. Reference lacquer films were prepared and analysed by Py-GC/MS. Py-GC/MS experiments were carried out with a CDS Pyroprobe 2000 heated filament pyrolyser, attached to an Agilent 6890N gas chromatographer equipped with a 5975N mass spectrometer. FTIR spectra were obtained in a Thermo Nicolet Nexus 670 FTIR spectrometer coupled to a Continuµm IR microscope.

Results

Stirrups' red lacquer presents a m/z=108 mass chromatogram profile corresponding to *R. vernicifera* or *M. usitate* lacquer. The m/z=104 mass chromatogram profile revealed that the lacquer isn't from *M. usitate* tree, though it doesn't fit exactly the *R. vernicifera* profile. The red pigment was identified by Py-GC/MS as Cinnabar (HgS).

Cross-sections from each stirrup are different. Py-GC/MS analysis of an intermediate layer revealed the presence of 3-(pentadeca-8Z,11E,13Z-trienyl) catechol (Fig. 1), which is the most abundant catechol of uncured *R. vernicifera* lacquer.

Conclusions

When studying the production technique of a work of art, sometimes is difficult to differentiate materials originally employed from those applied in a restoration, leading to imprecise conclusions. In this case, it was possible to understand how stirrups were originally lacquered. Py-GC/MS analysis indicated that the lacquer of an intermediate layer from the left stirrup has not cured properly, and thus all the above layers are not original. Lacquer's origin was also confirmed, but some difficulties arose in its identification. There may be an influence of cinnabar in lacquer curing mechanisms or ageing process affecting the m/z=104 mass chromatograms profiles.

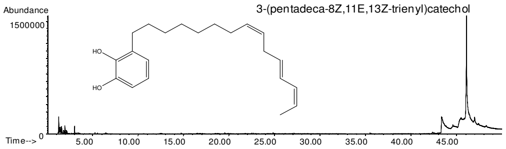

Figure 1: *TIC of an intermediate layer from the left stirrup*

Acknowledgements

This project was supported by Fundação para a Ciência e Tecnologia (PhD grant SFRH/BD/27573/2006). The authors wish to thank Prof. Miyakoshi (Meiji University) for the lacquer references.

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IDENTIFICATION OF COLOURING MATTERS IN TEXTILES FROM THE MONASTERY OF SIMONOS PETRA (MOUNT ATHOS)

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Introduction

Mount Athos has been an Orthodox spiritual centre since 1054 and has enjoyed an autonomous status since Byzantine times. Today, the "Holy Mountain" is still a major centre of the Christian religion with over 20 large, occupied and active monasteries. Peerless artworks of inestimable religious, spiritual and historical importance have been guarded by the monasteries for several centuries. Among them, important textiles can be found which have been barely studied [1].

A multi-disciplinary approach will be employed within the activities of the Byz-tex-Athos project, to study in detail thirty artworks from the Monastery of Simonos Petra (IMSP) which correspond to a long historical period (16th – early 20th cent.). The project is composed of the following phases: (i) clarification of the dyeing technology; (ii) stylistic and historic investigation; (iii) documentation and (iv) conservation of the historical objects. Preliminary results collected with respect to the first goal of the Byz-tex-Athos project are described in this study.

Experimental

Each microsample extracted from a textile artwork is treated with a solution mixture of H_2O:MeOH:37% HCl (1:1:2, v/v/v) for few minutes at 100 ^{0}C. The solvent is then evaporated to dryness under gentle nitrogen flow. The dry residue is dissolved in DMF and subjected to HPLC.

Results

Figure 1 shows the results obtained for the sample extracted from the ecclesiastical garment (sakkos) of Bishop Neilos Esfigmenitis (18th cent.) [2]. Fisetin, sulfuretin and quercetin are identified, suggesting thus that *Cotinus coggygria* Scop. (young fustic) was used during dyeing. Other, flavonoid components of young fustic are also detected. The structures of these compounds have been previously elucidated by LC-MS and NMR [3]. A complete analytical study of the thirty textile artworks from IMSP is currently under progress.

Conclusions

The biological sources of the dyestuffs used during dyeing of post-Byzantine textiles from Mount Athos (including textiles from IMSP) are unknown. Knowledge is mainly based on tradition rather than scientific evidence. Consequently, the identification of the origins of the dyes through elaborate physicochemical instrumentation is expected to provide valuable information. For example, it is interesting to note that young fustic, found in the sakkos of Bishop Neilos, was previously identified in ecclesiastical garments of the Western Church (13th cent.) [4], showing thus the interaction between Eastern and Western ecclesiastical art.

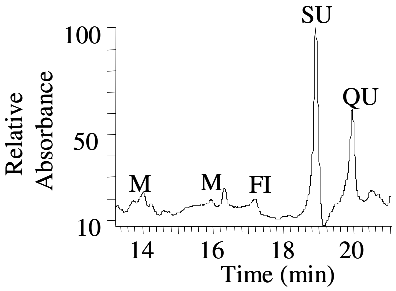

Figure 1. *HPLC profile of the historical sample extracted from the sakkos of Bishop Neilos. Identifications of fisetin (FIS), sulfuretin (SU) and quercetin (QU) are shown. Other minor, flavonoind components (M) of young fustic are detected.*

Acknowledgements

This work is funded by the Getty Foundation, CA, USA, through the Byz-tex-Athos project.

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AN ANALYTICAL STUDY OF INKS

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Introduction

Pyrolysis coupled to GC/MS allows the characterization of materials such as waxes, resins, oils, proteinaceous binders, amber, synthetic polymers, etc [1-4]. Pyrolysis is particularly useful in the artistic field because even if it is a destructive technique, it needs only a small quantity of sample. The aim of this work is to study detailed chemical composition of inks and inks on paper using PY/GC/MS technique.

Experimental

The pyrolysis characteristics of inks were investigated using a Gas Chromatography and Mass Spectrometry (Py-GC/MS). Details on the experimental conditions are given in ref. [5,6]. The inks were prepared following medieval recipes and contain in their composition seeds or peel of pomegranate, carnation, henna, saffron, apricot gum, arabic gum, gall nut, etc. Two kinds of inks were carried out based on vitriol and carbon (powder of grapevine).

Results

In the analysis of ink containing carbon the main peaks were furfural(4), butyrolactone(9), 5-furancarboxyaldehyde -5-methyl-(11) and 1,2-cyclopentanedione,3-methyl-(14). They derived from the degradation of arabic gum. The most intense peak was butanoic acid (3), which was not present in the pyrogram of arabic gum (Fig.1).

In the pyrogram of the same ink on paper the most intense peaks were butanedial (2), 2-cyclopenten-1-one (4), 2-cyclopenten-1-one,2-hydroxy- (9), 1,2-cyclopentanedione,3-methyl- (12), phenol,4-methyl- (13), 1,4:3,6-dianhydro-α-D-glucopyranose (15) and levoglucosan(16). All these compounds are produced by the pyrolysis of both cellulose and arabic gum, except for 1,4:3,6-dianhydro-α-D-glucopyranose which derives from cellulose only. In fact it was not present in the pyrogram of ink without paper, while the other compounds were present but in different amounts (Fig.2).

Conclusions

Pyrolysis is a useful procedure for the GC/MS analysis of the organic fraction in inks. The main advantages are the limited amount of required sample and the possibility to simultaneously analyze organic components belonging to different classes.

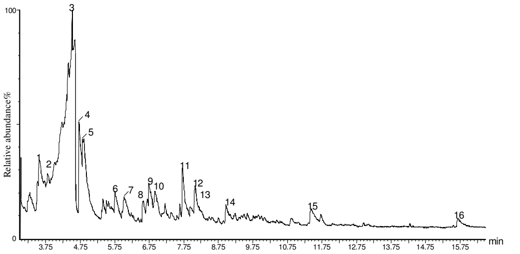

Figure 1. Pyrogram at 500°C of dried ink sample with pure carbon charcoal (powder of "grapevine") mixed with arabic gum, dissolved in water).

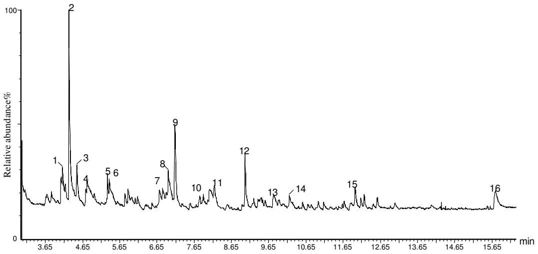

***Figure 2.** Pyrogram at 500ºC of the same sample on paper.*

Acknowledgements

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ARCHAEOLOGICAL CHERTS´ ORGANIC MATTER COMPOSITION ANALYSIS COMBINING GC/MS AND SPECTROSCOPY TECHNIQUES

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Introduction

Vibrational spectroscopic techniques (Raman and Infrared spectroscopy among others), in combination with other elemental techniques as X-ray Spectrometry, demonstrate to be powerful analytical tools when the characterisation of archaeological chert samples is required [1].In nature, there is a link between the presence of organic matter and the origin of chert samples. In this sense, the characterisation of the organic matter content in chert samples using Gas Chromatography/Mass Spectrometry (GC/MS) is needed in order to obtain all the information about archaeological chert samples, as it can provide relevant data about source catchment areas, artefact displacement or the way in which the artefacts were employed.

Experimental

The analysed sedimentary cherts were collected from different rock formations of Cretaceous to Cenozoic age in the Vasco-Cantabrian region (Western Pyrenees), and were formed in continental, shallow-marine and deep-marine depositional settings.

For the determination of organic content different analytical procedures were used in order to extract information about soluble (bitumen) and insoluble (kerogen) organic matter. Bitumen was extracted with dichloromethane using ultrasound focused energy and then analysed by means of retention time locked GC/MS. This way we were able to obtain qualitative results from the direct comparison of chromatrograms [2].

According to the content of insoluble organic matter, the isolation of kerogen was conducted by the standard hydrofluoric acid/hydrochloric acid extraction procedure [3]. Further treatment of the isolated kerogens involved ultrasonic extraction with dichloromethane in order to remove any residual trapped bitumen and then were analysed by means of Attenuated Total Reflectance Spectroscopy (ATR). The measure conditions were 4s, 40 accumulations and a spectral resolution of 4 cm^{-1} in the spectral range of 600-4000 cm^{-1}

Results

Chemometric analysis of the obtained results by means of Principal Components Analysis allows observing differences between hydrocarbon contents depending on the chert´s depositional settings. According to this, it seems that continental depositional samples have preserved more organic matter with little alteration. Moreover, the hydrocarbon profiles are dominated by high molecular-weight ($>n-C_{25}$) n-alkanes, alkyl and methylalkylcyclohexanes and isoprenoid groups.

On the other hand, direct measurements of isolated kerogen samples carried out using ATR spectroscopy, showed the kerogen´s characteristics bands at 2920 cm^{-1}, 2850 cm^{-1}, 1700 cm^{-1}, 1600 cm^{-1} and 1200 cm^{-1}.

Conclusions

The organic analysis of archaeological chert samples could be a powerful strategy in order to explain the origin and transformations of cherts. In this way, different geological contexts have been studied and distinguished. However, more quantitative analyses are required in order to quantify organic composition and the origin of the organic matter present in the chert samples.

Acknowledgements

This work was supported by.the Research Project CGL2008-00009/BTE and HAR-2008-05797/HIST of the Spanish Ministry of Science and Innovation, M.Olivares is grateful to the University of the Basque Country for a PhD. Fellowship.

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CHEMICAL INVESTIGATION ON THE BLACK PIGMENTS IN THE CARVED DECORATION OF ALABASTER TOMBS (16^{TH} AD) FROM ZARAGOZA (SPAIN)

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Introduction

Black or very dark pigments are often used or observed in the decorations of artworks, but their origin and composition could be sometimes not very clear, especially when they can be of organic nature and undergone a restoration. Carbon-based blacks are found in many artistic expressions, but other pigments like bitumen, tar, pitch and resin have been also documented [1,2]. Within the framework of a project on the study and restoration of several alabaster objects from the Museum of Zaragoza (Spain), the origin and possible reactivity of the pigments used in the carved inscriptions of some panels of two alabaster tombs dated from the mid 16th c. AD were investigated.

Experimental

An analytical protocol based on optical microscopy (OM), scanning electron microscopy (SEM), analytical pyrolysis in the presence of hexamethyldisilazane followed by gas chromatography/mass spectrometry (Py-GC/MS) and gas chromatography/mass spectrometry after alkaline hydrolysis, solvent extraction and trimethylsilylation (GC/MS) was used for the chemical characterisation of the microsamples from black inscriptions collected from the two alabaster tombs. Py-GC/MS and GC/MS analyses were performed using establishing protocols described in detail in ref. [2,3,4].

Results

OM and SEM analyses evidenced the presence of an amorphous very dark-brown substance, from translucent to opaque, constituted mainly by C and O, thus highlighting the organic nature of the material used in the manufacture of the inscriptions. Py-GC/MS and GC/MS analyses provided detailed molecular compositions (Fig. 1), highlighting the presence of a wide range of compound classes including diterpenoid acids (di-dehydroabietic acid, dehydroabietic acid and 7-oxo-dehydroabietic acid), tricyclic abietanes with a high degree of aromatisation such as retene, mid- and long-chain monocarboxylic fatty acids, n-alkanols, and n-alkanes. Characteristic biomarkers and their distribution patterns indicated that a mixture of pine pitch and beeswax was used in the production of the black inscriptions.

Conclusions

In both alabaster tombs, the carved inscriptions were filled using a mixture of pine pitch and beeswax. In fact, resins were often mixed with waxy materials in order to harden and colour the material. The technique resulted in a very dark decoration which stands out from the white alabaster.

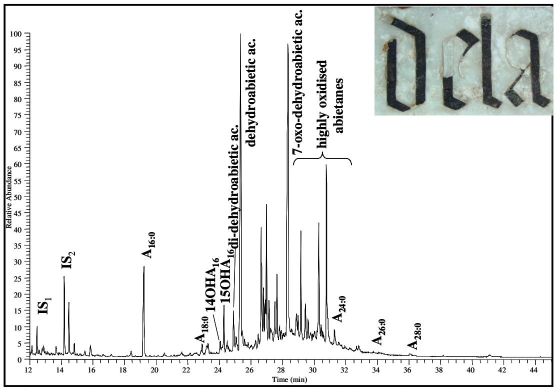

Figure 1: *TIC of the trimethylsilylated acid fraction of sample M30 obtained by GC-MS. $A_{X:Y}$ are fatty acids of chain length x and degree of unsaturation y; $XOHA_X$ are hydroxy fatty acids of chain length x and with hydroxy group at position X; IS_1 and IS_2 are the n-hexadecane and tridecanoic acid internal standards (inset: part of the black inscription)*

Acknowledgements

J. Pérez-Arantegui acknowledges the Spanish Ministry of Science (Subprograma de estancias de movilidad de profesores e investigadores: PR2007-0506 and PR2008-0362).

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TRANSMISSION ELECTRON MICROSCOPY FOR DETECTION OF MELANIN GRANULES IN ARCHAEOLOGICAL WOOL FIBRES

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Introduction

Archaeological wool and hair fibres from wet and waterlogged environments are sometimes so red in appearance that a dyestuff is expected to be responsible for the colour. Since dyestuff analyses using TLC and HPLC-PDA have not yet given any results, other causes, like natural pigmentation, has been considered. However it can be difficult to detect if melanin granules are present in archaeological fibres when observing the fibres in transmitted light microscopy. Cross sections may suggest that melanin granules are present, but it can be tricky, and it is neither possible to see if the granular are intact, nor determine the kind of melanin present. Mammalian melanin's exist in two forms: the brown to black eumalin and the yellow to reddish-brown phaeomelanin, The latter is relatively stable under extreme environmental conditions, the former is far less so [1]. Thus if only phaeomelanin is present in fibres this could be an explanation for the red colour. It is possible to see the melanin granules in TEM and it is also possible to detect if the grains are still intact or completely deteriorated [2]. This article investigates whether it is possible to identify melanin granular in archaeological wool fibres and if they are still intact.

Experimental

Two samples of red wool thread from Danish Iron Age burial (100A.D.) were prepared for TEM analysis. One sample followed the same fixating procedure used for plant material; the other was directly embedded in Spurr. Cross sections 1µm thick were cut and dyed with Toluidin blue prior to observation in Transmission Light Microscope (TLM) Olympus BH-2. Cross sections 50 nm were cut on a Reichert-Jung, SUPER NOVA Ultramicrotom and stained with lead and uranyl salts before examination in the TEM. Sample directly embedded in Spurr could not be cut due to soil content that would ruin the diamond knife.

Results

TLM showed that the 2000 year old wool fibres resembled new wool with ortho and para cortex, showing the same characteristics concerning dye acceptance. A more intense colouring of the ortho cortex with its more open and chemically reactive structure compared to para cortex (Fig. 1). Electron microscopy revealed that melanin granules were visible and intact in wool fibres. It was not possible to distinguish between eumelanin and phaeomelanin in cross sections (Fig. 2).

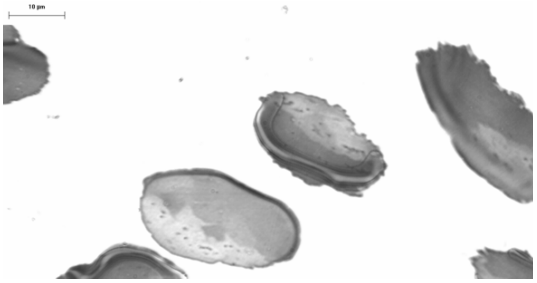

Figure 1: *TLM of 2000 year old fibre, showing a more intense colouring of the ortho cortex.*

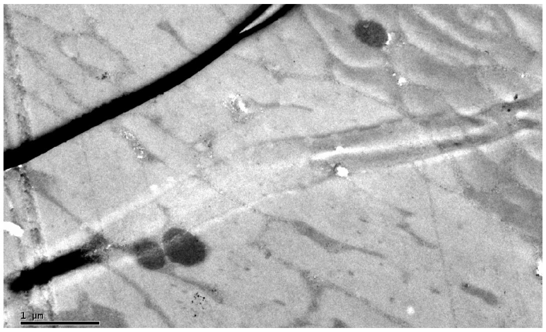

Figure 2: *TEM of 2000 year old wool fibre with 3 melanin granules: 2 in para and 1 in ortho cortex.*

Conclusions

It is possible to detect melanin granules in TEM analyses. The melanin granules seem to be intact, and there are no empty spaces indicating a deterioration of eumelanin. The red colour therefore cannot be explained by a loss of eumelanin. Further work has to be done in order to determine the content of respectively eu- and phaeomelanin

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CHARACTERIZATION OF TURIN POMEGRANATE FOUNTAIN’S COATINGS

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Introduction

The Pomegranate Fountain from Torino represents a tree with oak leaves and pomegranate fruits. The fountain was made in 1911 for the National Fair Trade in Rome as a copy of the Pomegranate Fountain from Issogne (XVI century), and in 1926 was placed in the Borgo Medievale of Turin. The fountain is made of different steels and the surface is covered by a thick layer of coatings, in order to protect and decorate the metal.

This artwork is not in its best conservation conditions: actually the coatings are partially cracked and the metal is widely oxidized. The fountain was subject to a number of restoration works and required repair in order to adapt it to the aesthetics of the period. Most of these restoration works went undocumented, but examination and analytical studies identified them. In order to project the new conservation methodologies, scientific analysis have been performed on the fountain. The aim of this project is the identification and the characterization of the coating’s stratigraphy of branches, leaves and pomegranates decoration.

Experimental

Micro- samples, taken from different parts of the fountain, were embedded in epoxy resin, observed with an Optical Microscope (OM) and analyzed by Scanning Electron Microscope (SEM) associated with a microanalysis EDX and by Fourier Transformed Infrared Spectroscopy in micro-ATR modality. Few samples were analyzed by Pyrolysis Gas Chromatography Mass Spectrometry (Py_GC/MS).

Results

The thick stratigraphy highlights the successively overlapping of new coatings without removal of the previous finishing.

Many layers of coloured coatings are present. They differ in filler composition and granulometry used in order to obtain the required colours for leaves and branches. Recent layers have been recognised by Py_GC/MS as commercial alkyd resins.

Three different layers of minium have been recognized. They differ in composition and granulometry, according to different technique of production. The ancient minium is a mixture of Pb_3O_4 and $BaSO_4$. The other two minium-layers are characterised by the presence of chrome red and calcium respectively.

The pomegranate fruits present a gold leaf finishing even if below there are many pigmented layers, used in the past interventions, in order to simulate or to emphasize the gilt.

According to Carlo Nigra the fountain is painted “with its natural colour” and the original layer is still present in few samples. It has been identified as a mixture of siccative oil, mineral pigments and proteinaceous materials.

Conclusions

Micro-destructive analyses shed light on coating’s stratigraphy. Many layers of coloured coatings are present and three different layers of minium have been recognized and characterized. The original layer has been identified and recognised as a mixture of oil and proteinaceous material. The more recent layers are commercial alkyd resins with different kind of fillers to obtain the required colours.

Acknowledgements

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ANALYSIS OF ARCHAEOLOGICAL TRIACYLGLYCERIDS USING LIPIDOMIC TECHNIQUES: APPLICATION TO 5TH C. BC-4TH C. AD LAMPS

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Introduction

This work presents a methodology based on nanoelectrospray and Fourier transform mass spectrometry to identify triacylglycerids (TAGs) in archaeological samples. The archaeological TAGs identification needs adapted sample preparation protocols to trace samples in advanced degradation state. The detailed procedure includes extraction of the lipid components from finely grinded ceramic using dichloromethane / methanol mixture and additional ultrasonication treatment and TAGs purification using a diol cartridge. The TAGs ionisation yield was increased by formation of lithiated adducts. The high mass accuracy and high mass resolution of the Fourier transform analyzer provide TAG MS and MS/MS profiles with mass accuracy below 1 ppm presenting easier data interpretation. The analytical approach is based on the implementation of "in-house" species-dependant TAG database using MS and InfraRed Multiphoton Dissociation (IRMPD) MS/MS spectra; several vegetal oils, dairy products and animal fats TAGs were studied. The access to the native structure of the lithiated TAGs using MS and MS/MS profiles brings more valuable information allowing distinction between oils, fats and dairy products from different origins (plants, fishes, mammals, etc.).

Experimental

The modern products constituting the database are chosen according to the vegetal species cultivated and the animals bred in North-Mediterranean regions. The adipose fats are sampled from freshly slaughtered ox, veal, lamb and pork, from subcutaneous tissues and from solid fatty tissues enveloping kidneys. Lanolin, a product made regionally from lamb wool, was bought in an herbalist in Cairo. Nine lamps are selected amongst the material excavated from the settlement of Olbia (Ukrainia) by J. Munk Høtje (Årrhus University, Danish National Research Foundation's Centre for Black Sea Studies, Denmark). The studied sector consists on the living quarter of the Lower City, occupied from the 5th c. BC to the 4th c. AD. Because of the high degree of preservation of their lipidic compounds, six samples were chosen for analysis. The purified organic extract on diol SPE column was analyzed by nanoESI-Qh-FT-ICR MS and MS/MS. Lithium was added to the sample as doping agent for higher ionization efficiency in proportion of 2% lithium chloride.

Results

The developed MS/MS-based technique implemented with cationization of the lipidic extract using lithium ion induces a powerful enhancement of the sensitivity and selectivity of the analysis, inducing the possibility to apply the method to precious trace archaeological samples. The IRMPD spectra of the lithiated TAGs reveals 3-step-fragmentation reactions allowing the determination of each fatty acid moiety: (i) the loss of a free neutral fatty acid, followed by (ii) a second loss of a α,β-unsaturated fatty acid moieties, and the (iii) detection of a series of lithiated fatty acids. The access to the native structure brings more valuable information allowing distinction between oils, fats and dairy products from different origins (plants, fishes, mammals, etc.). Using adapted sample preparation conditions to trace samples in advanced degradation state, including lipidic extraction with dichloromethane / methanol mixture and additional ultrasonication treatment, purification using diol cartridge, the present analysis succeeds identifying the nature of fats used as fuel used in these 5th century BC to the 4th century AD Olbia lamps: bovine / ovine fats could be identified [1].

Acknowledgements

The Agence Nationale de la Recherche ANR-08-JCJC-0082-01. The Proteomics core facility and the FT-ICR spectrometer used in this study were funded by the European Community (FEDER), the Région Nord-Pas de Calais (France), the Génopole of Lille, the CNRS, and the Université des Sciences et Technologies de Lille.

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TD/CGC/MS AND FT-IR CHARACTERIZATION OF ARCHAEOLOGICAL AMBER ARTEFACTS FROM ROMANIAN COLLECTIONS (ROMAN AGE)

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Introduction

Romanian museums preserve a large number of archaeological amber collections. Considering that Romanian amber (Rumanite) has been known for a long time it is of great interest to find out if the fossil resin used in these objects is of Romanian or Baltic origin. Despite the fact that Rumanite keeps the attention of Romanian geologists, it remained poorly characterized in what physical and chemical methods are concerned. The present study is part of ROMANIT - a project recently started at the national level and aims to establish certain methods to be used to characterize / differentiate Romanian from Baltic amber. The analytical techniques considered include TD/CGC/MS (thermal desorbtion / capillary gas chromatography / mass spectrometry) and Fourier Transform Infrared Spectroscopy, in transmission and variable angle reflectance (FTIR-VAR).

Experimental

Markes "UNITY" Thermal Desorber equipped with a General Purpose Hydrophobic Trap was used for direct TD of volatile organic compounds (VOC) trapped in fossil resin matrix. An Agilent GC 6890N equipped with a 25 m x 0.25 mm HP-5ms column was used with a temperature programme of 2 K/min ramp from 40 to 250ºC. MS detection was made with Agilent 5975 inert MSD in fragmentation mode by electron ionisation at 70 eV, data acquisition in SCAN mode 35 - 700 amu.

All FT-IR spectra were collected on a Bruker Tensor 27 and analysed at a 4 cm^{-1} spectral resolution. FT-IR samples about 1 mg were embedded in potassium bromide (1:10 w/w), pressed in a 3 mm diameter pellet and analysed in transmission. For FTIR-VAR samples were fixed on a gold mirror without any pre-treatment.

Results

Using in-house databases of VOC detected in controlled geological origin ambers, archaeological samples were screened for the biological markers which could be correlated with geological origin. The occurrence of such biological markers was further correlated with the "Baltic shoulder" presence (1250-1175 cm^{-1}) in the FT-IR spectra (figure 1).

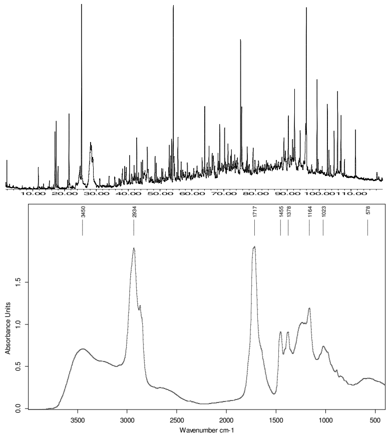

Figure 1: *TD/CGC/MS TIC, and FT-IR spectra of an archaeological artefact identified as Baltic amber*

Conclusions

TD/CGC/MS and FTIR could be successfully used for geological amber characterization. Even if some analytical criteria to differentiate Romanian from Baltic ambers were established [1, 2], their use on archaeological amber artifacts was not always successful. This may be due to chemical degradation in archaeological material. Further studies to establish the limits of TD/CGC/MS and FTIR as well as development of new analytical techniques would be worthwhile for unambiguous attribution of geological origin for archaeological amber artifacts.

Acknowledgements

This work was funded by the ANCS, ROMANIT project, contract no. 91-091/2007.

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ANALYSIS OF PIGMENTS AND ORGANIC MATERIALS FROM AN EGYPTIAN COFFIN (XXVI DYNASTY)

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Introduction

The polychrome wooden coffin (XXVI Dynasty, 664-332 B.C.) was made for Shepsesptah, a priest in Sechem, and was acquired in 1930 by Museo Ducale of Parma for wish of Mary of Austria, Duchess of Parma and Piacenza. It is an anthropoid shaped coffin, probably in *Ficus sycomorus*, with a gold gilded head mask and a gold and blue headgear. Shepsesptah wears broad collars, made of layers of floral multicoloured necklace. Under the necklace there is the representation of Nut, the goddess of the sky and of the vault of heavens, with opened wings and the sun disk on her head. The rest of the coffin is decorated with hieroglyphics inscriptions reporting chapter LXXII of the Book of the Dead. In 1962 it was restored for the first time. A recent restoring operation permitted the analysis of original materials as well as of already restored areas. It was all performed in the Museum, beyond a glass wall while the coffin was on display, so that the visitors could see all the restoration stages. The analyses we report have been integrating part of this last restoration.

Experimental

Pigment determination was performed both *in situ* exploiting a portable EDXRF spectrometer (Lithos 3000) and in laboratory on microscopic samples through a micro-FTIR spectrometer (Jasco IRT-3000) and a micro-Raman spectrophotometer (Jasco TRS-300).

Organic materials have been sampled and analysed by the GC-MS instrument Shimadzu QP 5050 and the FTIR spectrometer already mentioned.

Results

For each colour present on the coffin decoration, the corresponding pigment has been characterized, also examining those zones restored in the sixties. Moreover, the analyses on the pigments permitted to determine the pictorial stratigraphy with particular attention to golden gilded areas.

Through GC-MS and FTIR different organic binders such as beeswax and mastic were recognized.

Conclusions

The use of different analytical techniques allowed the complete identification of materials, which are all compatible with the period and provenance of the considered object.

Namely, as regards the pigments identified, we find calcium carbonate (used in Egypt as well as other natural white pigments), Egyptian blue (documented from IV Dynasty – III millennium before Christ, even if its discovery should be more ancient), orpiment (in use from the half of XII Dynasty), Egyptian frit and cinnabar (not attested in Egypt as ink, but probably imported, like minium, from about 1550 B.C.).

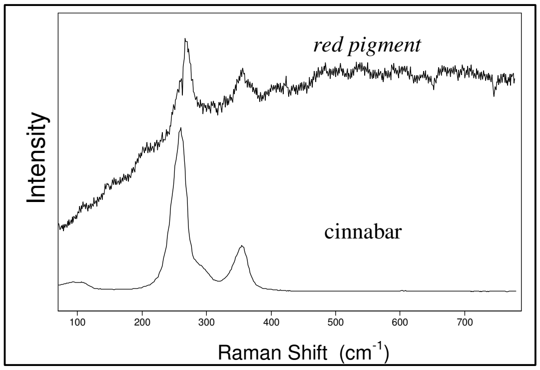

Figure 1: *Raman identification of cinnabar from coffin decorations.*

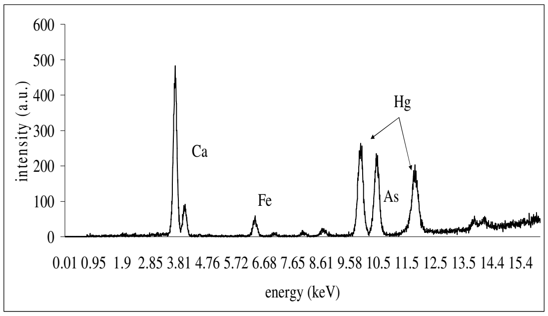

Figure 2: *EDXRF identification of cinnabar in coffin decoration.*

Acknowledgements

The analyses were performed during the restoration work made by T. Auricchio and A. Pilato.

PRACTICAL APPROACH TO THE IDENTIFICATION OF HISTORICAL SEMI-SYNTHETIC PLASTICS BY ATR-FTIR

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Introduction

In recent times majority of historical and artistic collections of the 19th and 20th centuries include a vast selection of semi-synthetic moulded plastics. In this group, there are plastics which are different in nature [1] and properties: vulcanized caoutchouc (Vulcanite, ebonite), cellulose nitrate (celluloid, parkesine), cellulose acetate and the casein formaldehyde (galalith, erinoid). Identification of plastics is the first step to avoid a degradation which is likely to occur [2]. This allows the conservator to develop the correct treatment strategies. Traditionally there has been employed some simple destructive tests (ex. dissolution, flame) which are not at all conclusive and requires sampling. The present work aims to investigate the reliability of the ATR-FTIR technique in the identification of the polymer blend [3], the surface-deposited degradation product [4] and the plasticiser loss that may occur during degradation.

Experimental

FTIR spectra were recorded using a Termo Nicolet 380 spectrometer (64 scans; 4 cm-1), equipped with an attenuated total reflection diamond crystal accessory. The analysed samples include several historical objects made of different type of plastics, all of them semi-synthetic and manufactured in the 19th and 20th centuries.

Results

The fig.1 shows some of the ATR-FTIR spectra obtained: a black button manufactured by Charles Goodyear in 1851 (a), the handle of a cutlery showing a severe cracking (b), one ivory-like fan (circa 1910) (c), and Spanish safety-film with a strong odour of vinegar (d).

The unknown plastics have been identified by comparing them with those from reference. Additionally to the polymer, the FTIR spectra show absorbances by all components of the polymer blends. Thus, the spectra show several peaks due to presence of additives, such plasticizers and inorganic fillers.

Conclusions

The identification of the different types of semi-synthetic plastics can be achieved by using ATR-FTIR. Since the complexity of the polymer blends, the spectra must be interpreted in light of the study of their historical and technological development.

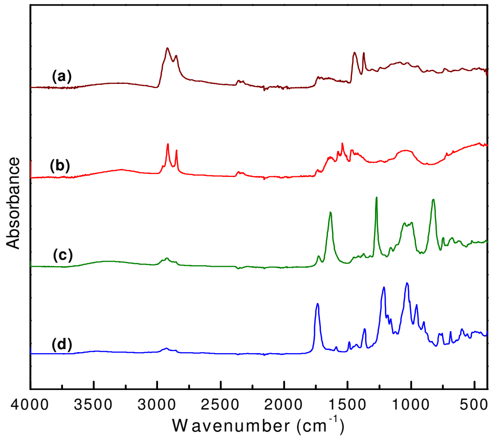

Figure 1: *ATR-FTIR spectra of the diferent types of historical semi-synthetic plastics. The objects can be identified as: Vulcanized caoutchouc [a], Casein formaldehyde [b], Cellulose nitrate, [c] cellulose acetate [d].*

Acknowledgements

This work was funded by the IV PRICYT de la Comunidad de Madrid and the Project CCG07-UCM/MAT-3002.

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NON-DESTRUCTIVE INVESTIGATION
ON A 17-th CENTURY DOCTOR DIPLOMA

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Introduction

A valuable manuscript, *Doctor Diploma,* from Padova, dating in 1633, brought in our laboratory with the view of conservation, give us the opportunity of analyzing the writing and decoration materials.

XRF and FTIR are the methods used in inks and pigments identification.

Experimental

The investigation of writing materials and pigments was carried out by analytical non-destructive methods, as: optical microscopy (Olympus SZ 60), XRF, FTIR.

The XRF was carried out on an InnovX portable apparatus, equipped with a Si(PIN) detector, with an Ag anode, the focal spot being of 2cm. diameter.

The apparatus used for FTIR analysis was a TENSOR 27 Spectrometer, Bruker Optics.

Results

The text of the manuscript is written with black ink and golden letters. The first file of the *Diploma* contains a rich colored miniature with green, blue, red, yellow, pink pigments.

We identified i.e. *Cinnaber* for red pigment (Fig.1), *gold* for yellow ink (Fig.2) and ferro gallic ink (Fig.3).

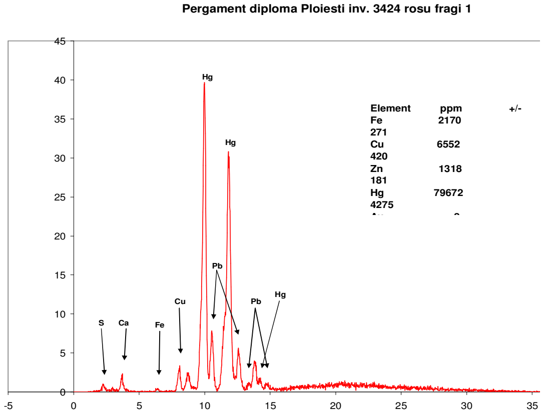

Figure 1: *Cinnaber XRF spectre*

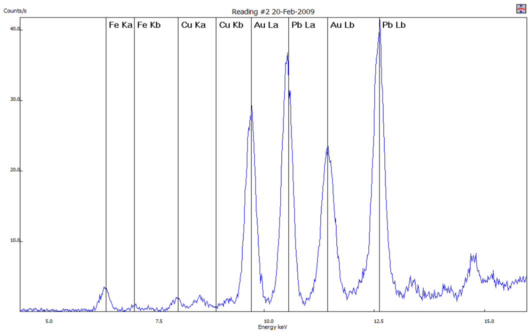

Figure 2: *Gold XRF spectre*

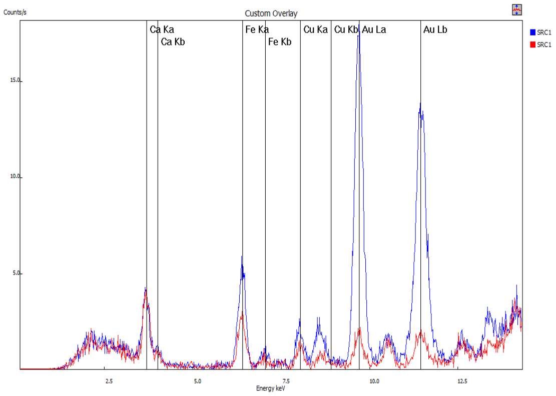

Figure 3: *XRF spectre – ink / parchment*

Conclusions

The results of present research complete the present-day knowledge about techniques and materials for writing and decoration foreign manuscripts from Romanian collections.

The results were compared with pigments identified on medieval manuscripts written in Romanian monasteries in order to headline the differences and the similarities concerning the materials and techniques of miniature.

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CHINESE EXPORT ART: MULTI-ANALYTICAL NON-INVASIVE CHARACTERIZATION OF 18TH-CENTURY PAINTINGS ON PAPER

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Introduction

A survey of the production of Chinese art specifically destined to foreign market is a peculiar and still poorly studied topic. Indeed, only a few studies have been published [1-4] that focus on scientific investigations of these artworks. A complete characterization of the composition and structure of this particular Chinese art would help both art conservators and art historians to identify the correct methods to be used for their restoration and to discriminate between original Chinese works and western imitations (chinoiserie). In the present communication, the analytical results obtained on five Chinese paintings belonging to the collection of Palazzo Pitti in Florence, different for content and style, will be presented. The pigments and dyes found in these works were characterized by using non-invasive techniques, micro-Raman, EDXRF and Fiber Optic Reflectance spectroscopy (FORS), exploiting the complementarity of the information obtainable by each of them.

Experimental

Raman spectra were acquired by using a Renishaw RM 2000 micro-Raman Spectrometer equipped with a diode 785 nm laser. Elemental compositions were found by using an Assing portable XRF model Lithos3000. UV-Vis-NIR reflectance spectra were collected by using two portable Zeiss spectroanalyzers models MCS501 and MCS511 NIR 1.7.

Results

In all but one of the paintings the traditional palette of the 18th-century Chinese pictorial art was detected. A rather peculiar blend of smalt, azurite and indigo was revealed on the blue areas of one of the investigated artefacts. The study confirms the complementarity of the three techniques and their efficacy in the investigation of Chinese pigments and dyes.

Conclusions

The results obtained improved the knowledge on the materials and techniques used for these artworks. Furthermore, these data could be used to compare the artistic materials used for export artworks with those made for Chinese domestic demand. The capabilities and limitations of the different techniques were also assessed by comparing the results.

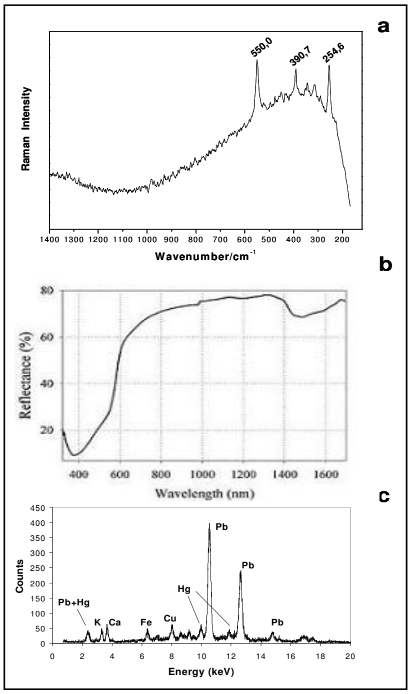

Figure 1: *Raman (a), FORS (b), and XRF (c) spectra acquired from the same red area of the GR 12359 painting. The pigments cinnabar (HgS) and red lead (Pb_3O_4) were identified*

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CELAS: STUDY OF A 16TH CENTURY POLYPTIC PANEL BY COMPLEMENTARY ANALYTICAL TECHNIQUES

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Introduction

The *Celas* polyptic, a 16th century composition of six panels from the Mosteiro de Santa Maria de Celas, Coimbra, was subjected to a detailed analytical examination for characterization and conservation purposes. The six panels, presumably requested from a painting studio in the North of France and executed ca. 1525, depict the following religious scenes: *Lamentation*, *Nativity*, *Assumption of the Virgin*, *Annunciation*, *St. John Baptist and St. Phillip*, and *Crucifixion*. The exhaustive study of this polyptic with several analytical techniques (with emphasis on Raman microscopy for palette recognition) aimed to characterise the original painting techniques and the subsequent restoration works through the 20th century. This case study also revealed the need for the use of complementary analytical techniques for a complete characterisation.

Experimental

Samples were removed, a minimum of 10 and a maximum of 18, in each panel, and were chosen to represent the colour palette of the polyptic. The samples were prepared as cross-sections, being embedded in a supporting medium, an epoxy polymeric resin. The main analytical techniques used were: Raman Microscopy (Jobin Yvon, LabRam 300, laser He-Ne 633 nm and solid state 532 nm), FTIR (Nicolet Nexus spectrophotometer with a Continuum microscope), micro X-ray fluorescence spectroscopy (μ-XRF, Intax GmbH, Mo anode), SEM-EDS (Zeiss DSM-962), and X radiography (ArtXray system). Other techniques include optical microscopy (OM) and dendocronology.

Results

The Celas polyptic is composed of six panels made of oak and a dendrocronology study revealed the oak came from the Baltic region. FTIR results showed the presence of animal glue and oil as binders. The ground layer was made with calcium carbonate mixed with the binder, being applied at least four times, following the technical traditions of Northern Europe [1]. Characteristic of this technical tradition one finds a layer of lead white over the calcium carbonate layers. OM and SEM-EDS revealed the components of those layers. The colour palette was identified by Raman microscopy, showing the use of a wide selection of mainly inorganic pigments, although a red lake was used extensively in all the panels. For the blues and greens copper pigments were the chosen ones (azurite and malachite, and in one panel, verdigris). Lazurite was identified in one panel (*Annunciation*), in agreement with the Flemish techniques of mixing this expensive pigment with azurite. The reds show a range of pigments that comprise vermilion, red lead and red ochres. Also the addition of a red lake, possibly madder, allowed the painters to explore different chromatic hues. Both types of lead-tin yellow and yellow ochre were identified. The black hues were not only made with carbon-based pigments but also with magnetite (Fe_3O_4) and umber (iron and manganese pigment). It was extensively identified by μ-XRF in all the panels. Some pigments from the restoration works were also recognized, such as blue phthalocyanine and viridian.

Conclusions

Complementary analytical techniques were used in order to have a full characterization of a 16th century polyptic, the Mosteiro de Santa Maria de Celas Polyptic. This study highlighted Raman Microscopy as a powerful tool for palette identification and to distinguish between the original painting and the restoration procedures. With the results of this study a restoration work took place and was finished in 2007.

Acknowledgements

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AN X-RAY MICROANALYTICAL STUDY OF RED GLOSS FINE WARE PRODUCED IN ANCIENT CASSOPE

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Introduction

Methods of X-ray microanalysis are well-suited for studying the provenance and manufacture of ancient pottery. Compositional characterization and grouping is achieved by X-ray fluorescence (XRF) spectroscopy. Production practices, such as the type of raw materials, the firing conditions and the surface coating techniques, are probed by X-ray diffraction and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX). In this work, an approach integrating the above techniques was used to characterize local production of red gloss pottery (2^{nd}-1^{rst} century BC) from Cassope, ancient Epirus.

Experimental

The 24 items of fine tableware included in this study were considered as local pottery on the basis of compositional data reported earlier [1]. Elemental concentrations were assessed through EDXRF spectroscopy. Selected sherds were examined using a D8 Advance Brüker diffractometer and a field-emission scanning electron microscope (SEM, FEI Inspect F) equipped with an EDX spectrometer.

Results

The EDXRF analysis showed the calcareous nature of the pots (Table 1). The use of Ca-rich pastes was probably deliberate due to the flexibility they provided to manufacture small vessels of various shapes and wall thicknesses. In addition, refinement with calcite prevented cracking upon firing, thus reducing the risk of failed products.

The main phases identified in the diffraction patterns were quartz (Q), plagioclase (P), K-feldspars (K) and diopside (D), while illite/muscovite (I/M) and secondary calcite (C) were present in some cases (Fig. 1). Based on the thermal decomposition and/or development of the above phases, firing temperatures between 900 and 1000°C were estimated.

SEM examination of the ceramic body showed extensive vitrification, which also implies firing in the range 850-1050°C. In general, the gloss layers were well vitrified, fairly regular with a varying thickness, scarcely reaching 10 μm (Fig. 1).

The EDX measurements indicated an excess of alkalis and a lack of alkaline earths in the surface gloss compared to the body. The gloss also exhibited a higher Al/Si ratio and Fe content. These findings suggest that the coatings were prepared by applying an illitic suspension to the main body before firing.

***Table 1:** Mean concentrations (M) and spreads (σ).*

	M	σ(%)		M	σ(%)
K (%)	1.51	19.1	Sr (μg g^{-1})	227	19.9
Ca (%)	6.80	31.0	Y (μg g^{-1})	23	15.0
Ti (%)	0.61	17.1	Zr (μg g^{-1})	135	15.2
Mn (%)	0.16	18.7	Ba (μg g^{-1})	230	18.1
Fe (%)	7.96	10.6	La (μg g^{-1})	15	21.1
Zn (μg g^{-1})	136	22.7	Ce (μg g^{-1})	36	10.1
Rb (μg g^{-1})	55	36.7	Nd (μg g^{-1})	10	17.2

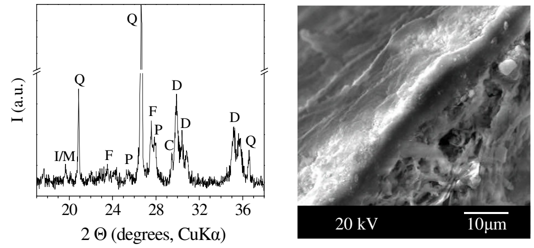

***Figure 1:** Left: Representative XRD pattern of a ceramic body. Right: SEM image of the same sherd, showing the body and red gloss surface layer.*

Conclusions

Employing X-ray microanalysis, technological features of red gloss pottery from ancient Cassope have been determined, including the selection and processing of raw materials used for preparing the body and gloss, as well as the firing regimes applied.

Acknowledgements

Measurements were carried out at the EDXRF and XRD units, UoI and in the SEM-EDX facility at the Institute of Materials Science, NCSR "Demokritos".

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THE RED PALETTE IN ROMAN VILLAGE OF *IESSO* (GUISSONA, CATALONIA-NE SPAIN): NON-DESTRUCTIVE X-RAY BASED ANALYSIS

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Introduction

Energy Dispersive X-ray Fluorescence (EDXRF) has become a powerful tool towards the obtaining of information about the chemical composition of pigments [1-5]. This work deals with the first application of EDXRF to the study of Spanish Roman wall-paintings. Red, which is common in Roman mural-paintings, is a colour that can have different origins. Most commonly used red pigments in the ancient Roman epoch were vermilion (*minium cinnabaris,* HgS), red lead (*minium secundarium,* Pb_3O_4) and red ochre (*rubrica*, Fe_2O_3) [6]. In our study, several red coloured fragments of wall-paintings related with the Guissona Manor House rooms have been analyzed in order to determine the inorganic elements of red tonalities as well as to characterize the supporting material.

Experimental

The analysed fragments include painted stuccos of the 2ond century A.D. from the excavations carried out during the 1996-1999 period. The red palette comprises shades varying from pale pink through to deep red. The elemental composition of all the samples was obtained by using a commercial bench top small-spot (0.1 to 3 mm) EDXRF spectrometer (XDV-SD, Helmut Fischer GmbH, Germany). Taking into account the limitations of the technique [7] other X-ray based methods (such as polarized optical microscopy (POM), X-ray Diffraction (XRD) and Scanning Electron Microscopy equipped with energy dispersive X-ray analysis system (SEM-EDS)) have been employed in some cases not only to confirm the results obtained from the EDXRF analysis but also to characterize the preparation layers.

Results

According to the elemental composition obtained by EDXRF, few remarkable differences have been found amongst the extensive gamut of red tonalities used in this site. Iron is present in all spectra. Furthermore, the presence of lead is detected in some samples.

In all cases the supporting material is composed by lime mortar (calcium carbonate).

Conclusions

The raw materials used are the most common employed in roman wall paintings. Red palette is mainly composed by haematite (we have found practically the whole range of colours given by this pigment).

The lack of highly prized red pigments (such as cinnabar) strikingly contrasts with a much more widely red palette found in the Northern Spain [8]. Local mineral sources seem to have been preferred in this village.

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USING NON-DESTRUCTIVE ANALYSIS OF PIGMENTS IN A STUDY OF AN 18TH CENTURY ICON

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Introduction

The characterization of cultural heritage materials is essential for the comprehension of their degradation mechanisms. To characterize and identify the pigments presents in religious painting (icons of wood support) of the 18th-19th centuries the collection of Cetatuia Monastery, Iasi.

Experimental

The goal of this.research was to know which pigments were applied in this artwork. For tthis study non-destructive techniques testing were used: X-Ray Fluorescence (XRF) and FT-Infrared Spectroscopy (FT-IR). The analyses have been made with the help of a portable X ray fluorescence spectrometer and FTIR spectrometer Vertex 70 Bruker, 30 – 25 000 cm^{-1}.The retable was analysed in 40 points.

The pigments applied were recognized on the bases of characteristic chemical elements from the XRF spectra. The comparison of the counts per second of different elements with regard to the background offers the possibility to obtain semi-quantitative results.

Table 1. *Summary of the XRF results*

Element	Line	Colour	Energy	Can be found in spectrum no.
Fe	K_α K_β	Blue	6.40; 7.06	5,9,12
Fe	K_α K_β	Grean earth	6.40; 7.06	3,4
Cr	K_α K_β		5.41; 5.95	
Zn	K_α K_β	White zinc	8.64; 9.57	2 -13
Pb	L_α L_β	White lead	10.5; 12.6	all
Ti	K_α K_β	White titanium	4.51;4.93	1-9
Au	L_α L_β	Gold	9.71; 11.4	all
Fe	K_α K_β	Red ochre	6.40; 7.06	1, 2, 6,7,8
Fe	K_α K_β	Yellow ochre	6.40; 7.06	11,12,13
Cr	K_α K_β			

Results

This comparison allowed the identification of protein peaks in all the icons study (N-H asymetrical stretching between 3400-3200 cm^{-1} and C-N stretching 1419-1004 cm^{-1} range).

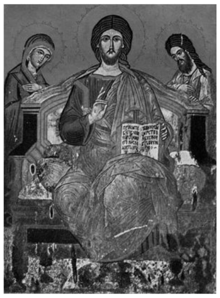

Figure 1: *Emperor Christ*

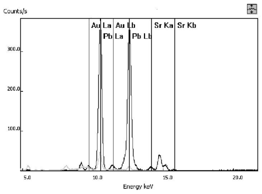

Figure 2: *Gold- XRF spectrum of the gilded Christ*

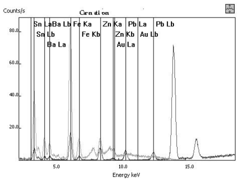

Figure 3: *XRF- spectra Original Carnation*

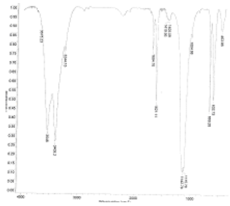

Figure 4: *FT-IR spectra for the identification of the pigment*

Conclusions

The pigments used originally are all commonly applied in the 18th-19th centuries: lead white, red ochre, green earth, yellow ochre, gold, blue Prussian and black organic. The presence Pb in all spectra shows that leat white was used also to lighten other pigments, as well as applied in the painting preparation and sometimes as a dryer. Chemical elements Ba, Zn revealed some later interventions with modern pigments.

Acknowledgements

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X-RAY FLUORESCENCE SPECTROMETRY CHARACTERIZATION AND TL DATING OF ANCIENT POTTERIS FROM BAN PONG MANOW PREHISTORIC SITE, CENTRAL THAILAND

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Introduction

Ban Pong Manow is the significant archaeological burial site in central Thailand where was in the 3,500-1,500 years ago. Natapintu [1] divided cultural periods into 3 stages; the bronze, early- and late iron ages by using the relative dating with artifacts. Thermoluminescence (TL) dating is one of many techniques used to date the pottery [2]. Six pottery shreds were collected for the XRD, XRF and TL dating.

Experimental

The analysed samples include 6 potsherds from two archaeological excavations were experimented by XRD, XRF and TL dating. The regenerative TL [3] technique was applied to date the quartz from the shred samples and the TL glow curve of PMN001 was shown in Fig. 1. The annual dose rate determinations were determined by gamma ray spectrometer.

Results

The XRD results presented the different mineral compositions in each potsherd from three cultural periods. The bronze-age sample (Fig. 2a) was composed of quartz, phlogopite, tremolite and grossular. The early iron-age sample (Fig. 2b) was consisted of quartz malachite, phosphophyllite and anorthite, showed interesting microstructures in each layer. The late iron-age sample was comprised of quartz, hematite and anothoclase. Six TL age results are shown in Table 1.

Conclusions

TL age, XRD and XRF results could divide into 3 periods; 1176 + 110 BC, 770 - 320 BC and 710 - 860 AD that are good conformed with Natapintu 2005 [1]'s interpretation by the archaeological evident.

Acknowledgements

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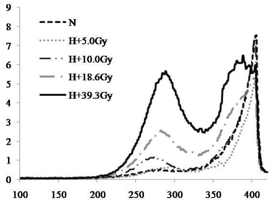

Figure 1: *TL glow curve of PMN001quartz sample: N - natural; H+5.0Gy – data for 5.0 Gy gamma ray irradiated to heated (320^{o}C; 5 hours) sample*

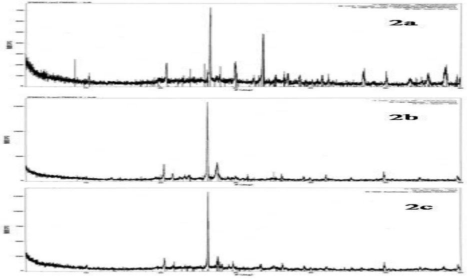

Figure 2: *XRD results of pottery sherds in each culture periods a) bronze b) early iron and c) late iron age*

Table 1: *Thermoluminescence data of pottery sherds*

	U(ppm)	Th(ppm)	K2O(%)	AD(mGy/a)	PD (Gy)	TL age (a)	TL date (a)
PMN001	1.6029	5.3628	0.7089	1.444	4.598	3184±320	1176±120 BC
PMN002	2.3334	7.6371	1.6687	2.566	5.98	2330±230	322±32 BC
PMN21	2.4497	8.0672	2.3862	3.211	3.676	1145±110	863±86 AD
PMN22	3.2595	9.1464	2.9232	3.918	5.059	1291±130	716±70 AD
PMN231	2.1175	6.2395	0.8938	1.779	4.678	2630±270	621±62 AD
PMN232	2.161	6.4193	1.8235	2.564	7.133	2780±410	774±115 AD

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ANALYTICAL STUDY OF AN EGYPTIAN AEGIS OF HATHOR

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Introduction

In the beginning of the 20th century, the Royal museum of Mariemont has bought a rather exceptional Aegis of Hathor, dated between the 22nd and 30th dynasty (Figure 1). With its 28 cm in height, it is one of the biggest Egyptian Aegis known at present. The outstanding technological production makes this object exceptional and has just recently attracted curators and scientists attention.

A closer view discovers an inlaid metal wire in the gorgerin and divulge a black appearance of the wig. The possible occurrence of Epyptian *Hśmn-km*, black patina, on this bronze statue , as pointed out in the literature (1), has certainly initiate this analytical investigation.

The aim of the study was to determine the metal composition of the various parts and search for possible intentional applications of coloured patinas.

Experimental

More than eighty different locations distributed over the Aegis were analysed non-destructively by a mobile µX-ray fluorescence spectrometer (ArtTAX, Bruker). Structure analyses were fulfilled by applying micro-Raman Spectrometry (Renishaw InVia) equipped with two lasers (λ=785 nm and 514 nm).

Results

Due to the numerous X-ray fluorescence analyses made along the Aegis, a tendency could be established in the variation of the different elemental compositions. The alloy used for the overall background of the gorgerin is composed mainly of copper, tin and minor of lead and antimony with traces (less than 0.2 %) of iron. The wire inlay has, compared to the back, a higher tin content but lesser antimony contribution (around 0.5%). This difference seems to be sufficient to cause a colour change of the metal.

Concerning the wig, the composition is comparable with that of the overall background of the gorgerin and no traces of elements as gold, silver or arsenic were detected. On the other hand, little remains of gold inlays at distinct places were found and were clearly intended to decorate the figure.

From the analyses also hematite inlays were established within the cavities of the crown of Hathor.

Conclusions

The study has demonstrated that non-destructive analysis by µXRF and µRaman can indeed reveal a lot of information about complex art objects.

Figure 1: *Image of the Egyptian Aegis of Hathor*

For this particular case, a search to parallel objects is needed in order to move on in the understanding of the inlaid, patination, colouring technology.

Acknowledgements

Françoise Urban is thanked for bringing the remarkable Aegis under our attention and for the encouragements during the analysis.

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DEVELOPING AN FTIR SPECTRA COLLECTION FOR INTERPRETING RESIDUES OF THE PREHISTORIC ACTIVITIES

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Introduction

Since the beginning of the 1940s, the classical way to interpret prehistoric stone tools function is the use-wear analysis which relies on the physical and chemical modification of the original flint surface due to the contact with the material worked which possibly leaves micro residues. The identification of their nature is of paramount importance in order to get additional light on the tool's use.

Up to now, residues analysis, carried out with different techniques, rarely faced to the subject by means of a systematic approach [1]. The not destructive micro FTIR technique was systematically used in order to identify the nature of micro-residues on archaeological samples through a comparison with a proper set of experimental tools. As an example of the results obtained, in this work the evidence of prehistoric hide working is presented.

Experimental

The analyzed samples consist of 88 experimental and 105 archaeological stone tools. Reflectance spectra were obtained using the last generation infrared microscope Hyperion (Bruker) in the frequency range 4000 – 600 cm^{-1} at a resolution of 2 cm^{-1} cumulating at least 200 scans. All samples were analyzed in areas not showing use wear alterations, in order to have a blank reference, and in all points showing use wear traces in order to check the existence of micro residues.

Results

The spectra of many prehistoric tools, interpreted as hide working implements by use-wear, showed a doublet at 1573 and 1537 cm^{-1} suggesting the presence of carboxy salt of adipocere which is the insoluble residue of fatty acid from pre-existing fats contained in decomposing hide. It is formed a couple of months after death by the slow hydrolysis of fats favored by the action of bacteria in wet conditions.

Identical spectral features were observed on experimental stone tools which worked the inner side of fresh hide, supporting the proposed assignment.

Conclusions

The presence of adipocere on archaelogical and experimental tools proves their use in the first step of hide working that is cleaning of *subcutis*. Moreover, the absence of adipocere suggests different hide working processes and/or unfavorable conditions to adipocere formation.

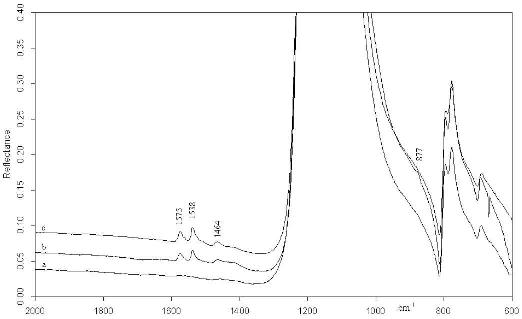

***Figure 1.** FTIR spectra of a flint tool without residues (a), archaeological flint tool used for hide working (b) and experimental flint tool which worked the inner side of fresh hide.*

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STUDIES ON NATURAL DYES: OPTICAL, MORPHOLOGICAL AND COMPOSITIONAL CHARACTERIZATIONS

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Introduction

Since prehistoric times natural dyes have been used for many purposes, but their use declined rapidly after the discovery of synthetic colours. Anyway, nowadays there is a growing interest, natural dyes being neither toxic nor polluting.

Natural organic dyes and derived lakes pose an interesting challenge to researchers since their identification is extremely difficult. Indeed, they are present in artifacts in very small concentration due to their very high tinting power.

UV-Vis reflectance spectroscopy permits the identification of dyes in a non-invasive way. In this work the chromatic properties of some selected dyes are investigated through the spectral reflectance factors. For a deeper insight of the dyes, Raman spectroscopy, Scanning Electron Microscopy and Energy Dispersive X-Ray analyses are used to return interesting compositional and morphological information.

Experimental

The analysed samples include five dye powders produced by means of traditional techniques at the Museo dei Colori Naturali (Lamoli, PU, Italy); madder, cochineal, weld, turmeric and woad were used to produce painted layers, too.

A fibre optics reflectance spectroscopy (*FORS*) module (Zeiss *MCS-CCD*) and a contact spectrophotometer (Minolta CM-2600d) provided the spectral reflection factor (*SRF*) and the colour coordinates of each model in the UV-Vis spectral range. Microscopy observations were made by means of a scanning electron microscope (JEOL *JSM*-6480*LV*) equipped with an *EDX* analyzer [1]. The Raman spectra were obtained by employing different excitation lines (λ = 442, 632.8, 785 nm); details are given in ref. [2, 3]

Results

The optical behaviours were investigated by acquiring the spectral reflectance factors of powders and painted layers. The potentiality of reflectance spectroscopy in discriminating the chromatic properties is shown in figure 1 where *SRF*s of weld and turmeric evidence the spectral differences of the two yellow colours.

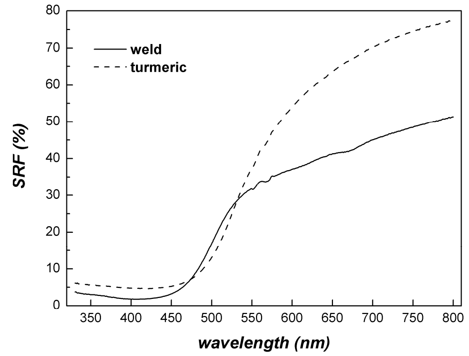

Figure 1: *Comparison of SRF spectra from weld and turmeric powders*

Characteristic features of Raman emission were observed from woad and turmeric. Whereas weld, cochineal and madder showed an intense background, due to the fluorescent typical of several natural dyes. The strongest Raman bands were just visible as tiny features on the background and the weaker ones were completely obscured.

Conclusions

Reflectance spectroscopy allows the identifications of dyes in a non-invasive way. SEM/EDX and Raman analyses can complete the characterization of the organic dyes when the fluorescent behaviour doesn't cover the vibrational emissions.

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IDENTIFICATION OF NATURAL WAXES IN POMPEII WALL PAINTINGS BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Introduction

Nuclear magnetic resonance (NMR) spectroscopy is an established, state of the art tool in many areas of applied analytical chemistry, especially when one has to deal with the molecular characterization of organic compounds. Even when one aims the challenging task of identifying specific compounds in complex mixtures, NMR can prove very successful [1], especially with the use of gradient 2D NMR techniques [2]. Our laboratory has undertaken the project of creating a spectral database of organic compounds of archaeological and historical interest [3], which can be used to identify these materials in works of art. The work that will be presented falls within the scope of this project and focuses on the identification of waxes in wall paintings from Pompeii. All the samples originate from the House of Marcus Lucretius [4] and they represent two different time periods.

Experimental

A number of wax samples were chosen so as to represent different reference materials. A series of one and two dimensional ^{1}H and ^{13}C NMR experiments were performed, as described in reference [1], in order to characterize the above samples, and contribute to the spectral database of reference materials built in our laboratory, which will be used for their identification in unknown samples of archaeological and historical interest. The proposed analytical methodology was subsequently applied to the unknown samples, which included organic top layers from wall paintings (4th-style) and painting fragments (2nd-style) excavated from the House of Marcus Lucretius at Pompeii [4].

Results

The different categories of natural waxes were easily discriminated by ^{1}H 1D and 2D NMR spectroscopy. Analysis of the Pompeii samples showed that the Fourth style paintings clearly contain a layer of beeswax, as depicted in Figure 1. However, the older, Second style samples do not seem to contain wax. Rather, the spectral data indicate the presence of resinous materials.

Conclusions

The beeswax detected in the Fourth style samples seems likely to originate from the first excavation period of Pompeii, at circa 1850 A.D., when protection of the wall paintings was attempted by these past conservators by applying a wax layer. Identification of the non-waxy organic components of the second style paintings is currently in progress.

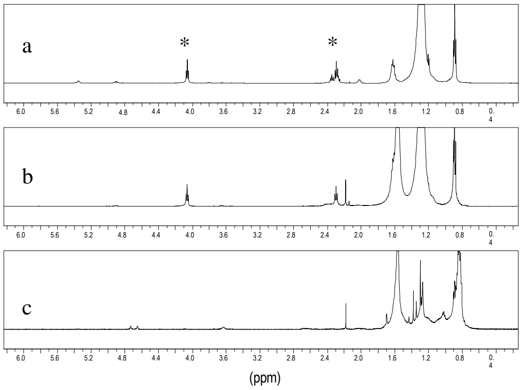

Figure 1: *^{1}H NMR spectra of beeswax (a), Fourth style wall painting (b), and Second style painting fragment (c), excavated from the House of Marcus Lucretius, in Pompeii. Asterisks (*) denote characteristic beeswax peaks.*

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IDENTIFICATION OF CULTURAL HERITAGE INORGANIC RED PIGMENTS WITH ATR-FT-IR SPECTROSCOPY IN REGION OF 500-230 CM^{-1}

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Introduction

In this poster we present that micro ATR-FT-IR spectroscopy in the low wave number range (500-230 cm^{-1}) can be well used for identification of those inorganic red pigments in the paint samples that contain simple anions like oxides, sulphides, etc, which often have no vibrations in the mid-IR range. Using the region below 500 cm^{-1} is the only way to identify these pigments by infrared spectra. Therefore reference samples of red pigments were prepared by mixing them with linseed oil. We demonstrate the usefulness of this approach with practical application examples on the cultural heritage red pigments, namely cinnabar (HgS), red lead (Pb_3O_4), and pigments based on iron (III) oxide (Fe_2O_3).

Experimental

The IR spectra were registered on Nicolet 6700 FT-IR spectrometer with CsI optics and "Smart Split pea" diamond micro-ATR accessory. Smart Split Pea is a horizontal single-bounce ATR micro sampling accessory with diamond crystal, angle of incidence of 45° and sampling area diameter of 500 µm. The spectral range available with this equipment is 4000-225 cm^{-1}. The reference samples of red pigments were mixed with linseed oil in approximately 1:1 mass ratio. Linseed oil was used because it does not have absorptions in the range of 500-230 cm^{-1} and mixing with red pigments gives much better results (lower noise, more intensive bands) in that region. The analyzed cultural historic object samples included red pigments of archaeological Pompeian wall paintings [1] and of Estonian coat of arms from 17th and 18th century. All pigment assignments made for the historic object samples using the ATR-IR spectra were independently confirmed using the SEM-EDS and EDXRF methods.

Results

All studied pigments have characteristic absorptions in the region of 500 to 230 cm^{-1} and can be easily distinguished from each other (See table 1). In the case of both HgS and Pb_3O_4 there is only a single pigment–vermilion and red lead, respectively. Anyhow there are a number of pigments having Fe_2O_3 (minerals hematite) as their main component (and also different additives). In the spectra of these pigments wave numbers of bands may shift somewhat depending on the pigment origin. Also hematite-based pigments can show variations in the position of the hematite bands in IR spectra due to differences in particle shape and size [2].

Table 1. *Characteristic bands wave numbers of red pigments in the region of 550-230 cm^{-1}*

Red pigment reference or CH Sample	Characteristic bands wave numbers (cm-1) in IR spectra
Vermilion	342, 284 (shoulder at 280)
Red lead	528, 454, 381, 328 cm-1 (shoulder at 318), 280
Natural red earth	537, 467, 431, 396, 366, 344, 276
Caput Mortuum, reddish	528, 458, 379, 294
Venetian Red	460, 422, 377, 354, 237
Pompeii red	534, 466, 428, 318, 272
Pink colour sample from the Ludwich von Tolli coat of arms (17th c.)	Read lead (Pb3O4): 530, 513, 453, 380, 312
Red colour sample from the Biestraum coat of arms (18th century)	Read lead (Pb3O4): 683, 527, 451, 441, 381, 326, 318, ~278 Vermilion (HgS): 344, ~282, 266
Red colour sample from the 4th style wall paintings of the house of Marcus Lucretius (before 79 A.D.)	Natural red earth (bands in the region of 550-230 cm-1): 537, 471, 433, 420, 397, 275, 250 (maybe 233)

Conclusions

We have demonstrated that ATR-FT-IR in the low wave number range (500-230 cm^{-1}) can be successfully used for self-made reference spectra of red pigments and for the identification of paint samples from historic objects.

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NANOLIMES EFFECTIVENESS ON CONSOLIDATION OF LIMESTONE FAVORED BY HIGH RELATIVE HUMIDITY

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Introduction

The compatibility and efficiency of the consolidation of decayed artistic (lime-bases wall paintings) and architectural (limestone) surfaces with nano-size particles of calcium hydroxide (slaked lime) was demonstrated by means of BET and SEM-EDX analyses [1]. There are also previous studies on defining the optimal conditions for storing slaked lime [2]. Results showed that slaked lime ($Ca(OH)_2$), when used as a building material, must be stored in a dry environment (RH-30%) to avoid carbonation. The nanolime carbonation process has also been recently investigated [3]. However, it was not clear yet the most suitable humidity conditions for the compatibility and consolidation of these inorganic treatments when applied to carbonate stone materials. The aim of the present work is to evaluate the effectiveness and the optimal humidity conditions of a consolidating product based on nano particles of slaked lime combining several non-destructive techniques (NDT).

Experimental

Several NDT: Environmental Scanning Electron Microscope (ESEM), Nuclear Magnetic Resonance (NMR) and mobile Optical Surface Roughness (OSR) analyses together with the determination of capillarity, water absorption under vacuum and propagation of ultrasounds velocities, were used to assess the effectiveness of a consolidating product based on nano particles of slaked lime. This product was crystallized in climatic chambers at 30% and 75% relative humidity to consolidate fresh samples of magnesium limestone typically used in historic buildings of Madrid (Spain). The samples were analyzed before and after consolidation.

Results

The high relative humidity conditions (75%) seems to favour the consolidation process as observed under ESEM, NMR and OSR analysis (Fig. 1), and quantified through capillarity, water absorption under vacuum coefficients, ultrasounds velocities and NMR and OSR analysis as well.

Conclusions

The non-destructive techniques (NDT) used in this research have shown to be fast, precise and a very useful way of evaluating the effectiveness of nanolime as consolidating product, where the environmental conditions of application are favoured by a high relative humidity. Specifically, the mobile OSR analysis allows observing and quantifying the surface evolution with by 3D images (Fig.1), being also possible to use it in situ in the field.

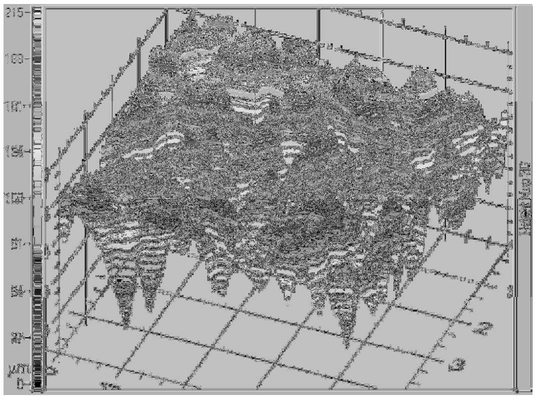

Figure 1: *3D image of the surface of magnesium limestone obtained under Optical Surface Roughness (OSR). Topo roughness optical values (µm), Ra: 8.73 ± 2.07; Rq: 11.18±2.54; Rz:34.97±7.61.*

Acknowledgements

This study was funded by the Government of the Community of Madrid under the project "Durability and conservation of traditional natural materials in heritage architecture" (MATERNAS CM 0505/MAT/0094) and the Spanish Ministry of Science and Innovation as part of the Consolider-Ingenio 2010 programme (CSD2007-0058).

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REMOTE SENSING AND DOCUMENTATION OF MOSAICS

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Introduction

Mosaics have an intrinsic three-dimensional structure due to finite size, shape, position and orientation of tesserae in order to produce particular effects by light reflection, formation of shadows, etc, as well as an extrinsic one since they are often located on curve surfaces such as vaults, domes, pillars and so on. Unfortunately, the usual photographic documentation does not account for these peculiar characteristics and propose a necessarily planar image of mosaics, thus neglecting important information that, in the case of surveys preliminary to restorations, for instance, is rendered in graphics by means of conventional notations.

Therefore, use of 3D laser scanner has been proposed to overcome these difficulties and provides archaeologists, art historians and museums keepers with suitable tools for a better knowledge and representation of mosaics [1]. The instrumentation here described has been utilized on samples and large mosaics such as those in the Basilica of St. Apollinare Nuovo in Ravenna (Italy).

Experimental

A main difficulty in this kind of investigation arises from lack of data in some regions in correspondence with tesserae borders and dark colour elements – in particular for black tesserae where the laser light is completely absorbed and dark green ones – resulting from the dominant glass material in mosaics composition since its lucid and compact surface reflects the light in such a way that it is only partly detected by the optical sensors of the instrument. This disturbing phenomenon is often generated in scanning bronze works, which - to overcome this limitation - were, in some cases, treated with powder or spray opacifiers provided their removability. It was considered necessary, in our case, sprinkle the mosaic surface of powder, thus making possible the acquisition of a sufficient amount of points from all the tiles.

In the attempt to compensate for any gap in the data cloud configured in the first scan tests, it was thought to capture the same portion of the surface several times, by inclining the laser emitter at different degrees. For these operations, the manufactured support which allows a shift (50 cm. x 35 cm.) was fixed to a rotable mechanical base, connected to the computer and operated directly by the software processing of the clouds of points, in order to define precisely the angle of inclination of the surface to be collected with respect to the scanner.

After completing the acquisition of the mosaic, taken to an inclination of 0°, 15°, 30°, 45° and 70°, respectively, it was made the realignment of the five resulting clouds of points. By means of the Poygon Editing Software Tool, supplied as a standard accessory to the scanner by Minolta, one has identified counterparts of the points in each cloud, to be aligned through suitable roto-translations. A subsequent merging feature has produced a single mesh of points, where the lack of information derived from the cloud at 0° scan is partially compensated by the superimposition of the other clouds.

Conclusions

This work, even still in progress, already allows one to outline a few useful remarks on the benefits granted by these investigations to the study of mosaic works. As for the scheduling of a real campaign of three-dimensional relief for mosaics of large dimensions, a few issues that could be solved thanks to the rapid evolution of these technologies have to be carefully planned as previously shown, resulting laser scanning a useful tool for documentation of mosaics.

The creation of virtual models of small portions, representing compositions where they belong, would permit to carry out comparative investigations of mosaic cycles, leading to quantify similarities and differences in terms of processing and surface rendering of the mosaics themselves. From the virtual model one can perform accurate measurements on the size of the tesserae, their distance, position and orientation, even their projection with respect to the support.

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THERMAL STABILITY OF PARCHMENTS BY MHT: A RELIABLE METHOD FOR GRADING DETERIORATION OF ARCHIVAL FONDS

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Introduction

Direct microscopic observation of thermal stability behaviour of collagen fibres in water has provided a standardised analytical technique, namely MHT method, which proved to be highly valuable for a broad range of research and conservation applications of skin and leather materials in museums, libraries and archives. To improve the content of information from the MHT method, correlation between shrinkage and DSC parameters is reported in this paper.

Experimental

New parchments, parchments exposed to chemical pollutants (50 ppm NO_x, 50 ppm SO_2), heat (100 °C) and visible light irradiation ($1.5\cdot10^5$ lx), as well as archival parchments (i.e. a group of 8 bookbindings in the Historical Archives of the City of Turin) were investigated.

Parchment fibre shrinkage activity and temperature were determined using a Caloris micro hot table controlled by a temperature processor coupled with a stereo microscope Wild Heergbrugg assisted by a home-made software [1].

DSC measurements were performed in both sealed crucibles in static atmosphere and open crucibles under gas flow at 25°C to 260 °C [2,3].

Results

A very good correlation between shrinkage temperature T_s and denaturation temperature T_d of collagen fibres was found for both new parchments (T_s=57.8±3.8°C and T_d=57.9±3.0°C) and artificially aged parchments (T_s and T_d paralelly decrease with ageing time and in function of the ageing factors). Heavily damaged samples showed substantial decrease of T_s until the shrinkage activity completely disappears. Combination of chemical pollutants and dry heat lead to the complete degradation of fibrillar structure after 4 weeks (Fig.1, 3rd & 4th histograms). This result should be ascribed to hydrolytic and oxidative processes causing heavy cleavage of peptide bonds and covalent crosslinks. However, for historical parchments comparison between T_s and T_d is limited by the high heterogeneity of deterioration. Correlation between other parameters determined by MHT and DSC can be used when the simple T_s analysis gives poor results. We found that departure of the final temperature of shrinkage interval T_{A2} from the temperature of DSC peak shoulder T_{peak2} increases with deterioration, whereas shorter departures between the starting temperature of shrinkage interval T_{A1} and T_{onset} of DSC peak indicate severe deterioration. For grading deterioration, scores from 1 to 4 were assigned to T_s, T_{A1} and T_{A2} values and averaged for each sample to obtain the damage level index S. Four levels of deterioration were selected for historical parchments: very small, $1< S <1.5$; minor, $1.5< S <2.5$; medium, $2.5< S <3.5$ and major for $S >3.5$ [3].

Conclusions

Comparison between parchments' grading based on damage criteria set up through shrinkage activity and that previously obtained using the more comprehensive DSC markers [3] has proved to be good (Fig.2), confirming the usefulness of employing MHT as basic tool for direct measurement of conservation state at curatorial level.

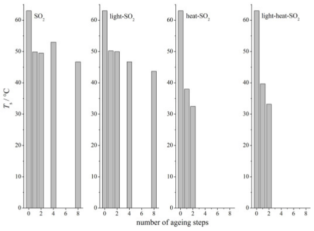

Fig 1: *Shrinkage temperature T_s change with ageing time (0 to 8 weeks) and factors (SO_2, light, dry heat and their combination)*

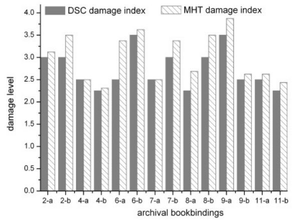

Fig 2: *Comparison of damage indices of 8 archival bookbindings obtained by both MHT (microscopic level) and DSC (mesoscopic level)*

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P76

CHANGES IN PAPER STRUCTURE DURING AGEING CAUSED BY FUNGI AS IT’S SEEN BY TIME-DOMAIN NMR

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Introduction

Valuable paper documents and artworks stored in archives are subjected to different ageing factors such as oxidation, UV radiation, atmospheric influence (dust, moisture, temperature), biological factor (contamination by bacteria, fungi, insects). One of the most effective destruction processes is produced by fungi that utilize cellulose and other paper ingredients in their bioactivity. Even if room humidity and temperature regime are kept within strict corridor to obey conservation standards in some cases during hundreds of years fungi colonies get to cover whole pages, irreversibly spoiling documents (Fig. 1). But as it’s seen at the same time some books at the same repositories turn out to be not affected by microbiologycal way. This evidently occures because of different chemical conditions within books. However that would be really great to detect potentially unsafe books on the early stages of spoilage when fungi layer is negligibly thin to be observed by eyes.

In the presented material we demonstrate the accurate possibility to get to know even slight content of paper mushrooms on pages by means of TD-NMR spin-lattice relaxation time and spin diffusion measurements.

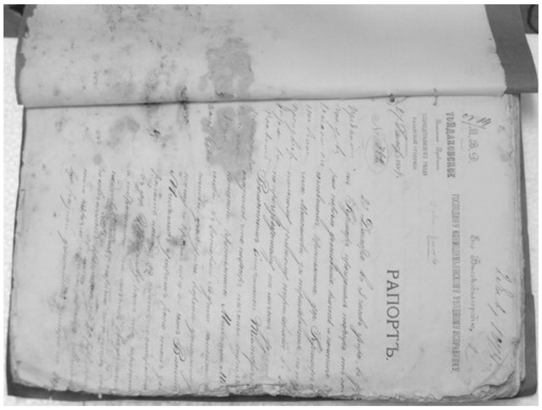

Figure 1: *Aged archive book destructed by fungi colonies*

Experimental

Samples

The samples, made from defective fragments of several archive paper documents of the middle of the 19 century, were investigated. It was prepared a series samples taken from pages regions with different fungal affection. All samples were NMR tested at 14 points of their adsorption isotherm from water activity from 0.045 to 1 p/p_s.

Measurements

Samples made from aged paper documents were investigated by TD-NMR. The measurements of spin-lattice relaxation time T_1, which appears the structural characteristic of the investigating object, was done using universal low-resolution NMR-spectrometer “Spin Track” [1] with resonance frequency of 19.2 MHz, probe diameter of 10 mm, 90°-pulse duration of 1.9 us, dead time of 8.5 us. Measurements of T_1 were taken for all points of sorption isotherms which were received for two types of samples. It was found that T_1 values of more defected by fungi samples for all steps of adsorption isotherm occurred to be lower in 50 percent on average in comparison with the suitable values of T_1 for samples made from clear regions of aged paper.

Results

Being highly active for adsorption not only of water vapor but various atmosphere chemicals fungi can be considered as extremely sensitive indirect indicator, because the T_1 of their cell structures and liquid content significantly changes once any such kind of adsorption occurs. Since fungi penetrate quite deep into the paper they are able to change spin-lattice relaxation of the amorphous part of cellulose, lignin and other paper compounds.

Conclusions

TD-NMR is sensitive method for determination of the degree of fungi contamination and it should be developed as the method of ageing degree estimation. In spite of obvious informativity this method requires the destruction of paper material for samples preparation. Assuming this it would be reasonable using handheld NMR sensor like NMR-MOUSE® [2], however sensitivity and recovering time of existing surface NMR sensors don’t allow receiving of well enough reproducible data signals.

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FURTHER APPLICATIONS OF FOURIER TRANSFORM INFRA-RED SPECTROSCOPY (ATR/FTIR) AND SCANNING PROBE MICROSCOPY TO PARCHMENT

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Introduction

The aim of this paper is to report on the further application of ATR/FTIR and scanning probe microscopy to damage assessment of archival parchment as developed in the IDAP project'Improved Damage Assessment of Parchment' [1] and then continued within the OPERA project "Old Parchment, Evaluation, Restoration and Analysis".

Experimental

ATR-FTIR spectra were recorded using a PE 2000 FTIR spectrometer with a TGS detector and a "SensIR Technologies" Durascope placed in the sample compartment. Scanning probe microscopy was performed using a JPK Atomic Force Microscope (Berlin, Germany) and an Explorer AFM sample base (Veeco, Santa Barbara, United States) modified with a µTA 2990 unit for localised thermal measurements (micro-TA). A more detailed description has been reported elsewhere [2]. Samples in the IDAP project included unaged reference samples, and those that had undergone accelerated ageing with dry and humid heat, light, and inorganic pollutants (NO_2, SO_2, mixed NO_2SO_2 under controlled conditions, also together with heat and light). These were tested together with historical samples from the following archives: Archivio di Stato, Florence, National Archives, Scotland, the Royal Library,the School of Conservation, Copenhagen, and the Municipal Archives in Segovia, Spain and in Turin and Genoa,Italy. All samples were initially evaluated using a visual assessment damage protocol developed in the IDAP project [1]

Results

ATR/FTIR spectra of archival samples from the grain side of the parchment were used for damage assessment. In IDAP it was found that for historical samples the ratio of absorbances at 1660 and 1630 cm^{-1} within the Amide 1 peak provided a means for ranking damage. The ranking obtained for over 50 samples was compared with that obtained from other techniques and in most cases correspondence was observed [2].

In this paper some examples from the archives of Turin and Genoa will be discussed in more detail with reference to the results obtained from scanning probe microscopy. Scanning probe microscopy provides a detailed description of collagen structure at the nano-scale level and the appearance and extent of periodic D-spacing is taken as a marker of the condition of collagen within the parchment. Micro-TA provides additional information on localised thermal behaviour of gelatinised areas within the collagen structure.

Conclusions

Differences in damage to collagen in parchment as recorded by ATR/FTIR and scanning probe microscopy were found to be influenced by the chemical composition and the preservation history of parchment, and how the parchment had been used (e.g manuscript or bookbinding). The effects of previous water damage and conservation treatment were also characterized. The comprehensive database obtained in the IDAP project was used to evaluate samples from the Turin and Genoan archives and which were provided within the context of Piedmont region research project "Old Parchment, Evaluation, Restoration and Analysis" (OPERA).

Acknowledgements

This work was funded by the European Commission 5th Framework Programme IDAP, Improved Damage Assessment of Parchment' (EVK4-CT-2001-00061).

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FOURIER TRANSFORM-RAMAN SPECTROSCOPIC STUDY OF A NEOLITHIC WATERLOGGED WOOD ASSEMBLAGE

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Introduction

The use of Fourier transform Raman spectroscopy in the field of lignocellulosics characterisation has increased significantly the last twenty years [1]. A FT-Raman spectroscopic study of changes in chemistry of waterlogged archaeological wood of *Pinus* sp. and *Quercus* sp. identified in an archaeological assemblage recovered from northern Greece is presented. FT-Raman spectral features of biodeteriorated wood were associated with the depletion of lignin and/or carbohydrate polymers at various stages of deterioration. In addition to spectra of archaeological wood a spectrum of sound wood of the same taxa was obtained. A comparison of the relative changes in intensities of spectral bands associated with lignin and carbohydrates as a result of decay indicated clearly extensive deterioration of both softwood and hardwood samples. The biodegradation of the archaeological samples followed a pattern of initial preferential loss of carbohydrates causing significant loss of cellulose and hemicellulose, followed by degradation of lignin.

Experimental

A selection of three oak and three pine waterlogged samples were analysed. Fourier-Transform Raman spectra were obtained using a Bruker IFS66 instrument with an FRA 106 Raman module attachment and Nd / YAG laser excitation at 1064 nm. Details on the experimental set-up are provided in ref. [2]

Results

The FT-Raman spectra of the archaeological oak sample (Fig. 1) identified that cellulose, hemicellulose, holocellulose, extractives and phenols were completely degraded, leaving a lignin (Indulin AT lignin) structure with little hemicellulose. The lignin was also affected to a great extent.

Conclusions

The spectroscopic study identified extensive deterioration of both the pine and oak archaeological samples. The biodegradation of the archaeological samples from Anargyroi III followed a pattern of initial preferential loss of carbohydrates causing significant loss of cellulose and hemicelluloses, followed by degradation of the lignin. These observed degradation features in the archaeological samples could be attributed to both fungi and bacteria.

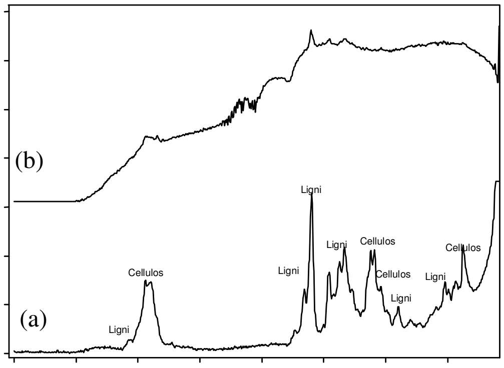

Figure 1: *FT-Raman spectra of the archaeological sample. For comparison reasons a sample of a fresh Quercus species sample (in this instance Quercus macedonica) was scanned and characteristic peaks of cellulose and lignin*

Acknowledgements

This research project was funded through a scholarship from the State Scholarships Foundation of Greece (IKY) and undertaken in the Division of Archaeological, Geographical and Environmental Sciences at the University of Bradford.

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AN INTEGRATE STUDY FOR MAPPING THE DAMPNESS DISTRIBUTION ON WALL PAINTINGS

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Introduction

Dampness is a major cause of decay to porous materials such as stone, brick, mortar and plaster as shown in the scientific literature of the conservation science. Accurate diagnosis of the cause and extent of damp is a fundamental step for preserving wall paintings. Nevertheless, the moisture distribution within a wall painting is difficult to determine. This paper shows the study performed on the frescoes in S. Rocco, Cornaredo (Milan, Italy). The church is seriously affected by moisture diffusion which causes damage to the frescoed surfaces. In this work the monitoring of dampness in the wall painting of this church has been performed using an integrated approach of unilateral NMR and IR Thermography (IRT), supported by the traditional gravimetric methods. The unilateral NMR technology is fully portable and can be directly applied *in situ*, without any sampling. In this study the results obtained by this portable and non invasive NMR technique are related to the results obtained with two conventional techniques used to detect and measure the dampness: the gravimetric methods and IRT. IRT is a non-contact, ND test that uses an infrared camera to detect and record infrared energy producing a thermal image of the object's surface temperature. Current IRT procedures [1,2] do not easily supply quantitative data of the water content, only the qualitative approach can be extensively applied. The simplest solution of quantifying moisture consists in the integration of IRT with the direct measurements of water provided by other testing, such as weighting tests, moisture probes, etc [3].

Experimental

NMR measurements were performed at 0.5 cm of depth in the plaster. Data processing allowed the obtainment of maps in which color gradients represent the differences of moisture content. On the same wall, author accomplished a preliminary thermal scanning, which allowed to detect colder areas. The researchers collected samples from these zones, and they measured the water content by gravimetric tests (UNI 11085).

Results

Recently we have demonstrated that the unilateral NMR can be successfully used to monitor the distribution of dampness in wall paintings [4].

In fact, the intensity of the NMR signal is proportional to the water content [5]. The map obtained by a suitable processing of NMR data allows an easy visualization of the distribution of the dampness. A proper calibration procedure with suitable specimens was performed to calibrate the NMR signal and therefore to obtain a quantitative evaluation of the moisture content. The comparison between IRT, NMR and gravimetric tests shows a good qualitative correspondence of the processed data. Beside to obtain the map of moisture diffusion on the surface, and underneath it, the integration of results also allows the hygroscopicity of the very exterior layer of the surface to be mapped.

Conclusions

The application of NMR shows its effectiveness in mapping moisture distribution: the resulting map is much more accurate and detailed than IRT map. This first set of measurement shows the effects of the interaction of different plasters and restoration products with the air at severe microclimatic condition (low temperature and high RH). NMR application is a consistent improvement to the study of thermo-hygrometrical behaviour of surfaces *in situ*.

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^{1}H NUCLEAR MAGNETIC RESONANCE AND ELECTRON MICROSCOPY STUDY OF THE HYDRATION PROCESS IN LIME-POZZOLAN MORTARS

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Introduction

The hydration process of lime-pozzolan mortars is essential for the development of their performance characteristics. During hydration, development of a hydrous gel takes place, consisting of various calcium aluminum-silicate hydrated phases (C-A-H, C-S-H). These phases are quite similar to those occurring in cements.

^{1}H Nuclear Magnetic Resonance (NMR) has been widely used to study the hydration process of cement. It is a powerful experimental technique that can be used to monitor non-destructively the micro-structural evolution in the paste as it provides details about its structure and dynamics at the molecular level. The hydration process is monitored by measuring the proton spin-lattice relaxation time T_1, which involves the exchange of energy between the spin system and its surroundings (lattice). This relaxation time is mainly related to the development of the surface area of the cement pastes and so it can be used to follow the hydration process [1, 2].

Aiming to widening further the application of the above technique, the objective of this work is to study the potential of the ^{1}H NMR to monitor the hydration process on a lime-natural pozzolan system. Furthermore, the development of the hydrated phases are studied by scanning electron microscopy (SEM), X-Ray diffraction (XRD) and thermal analysis (DTA/TG); and correlated to the results of ^{1}H NMR.

Experimental

The hydration process was studied on a lime-pozzolan paste, consisted of equal parts of lime powder ($Ca(OH)_2$) and a pozzolan. The pozzolan is of volcanic origin and has a grain-size in the range of 0-75μm. The water to binder ratio was set to 0.7. The setting mechanism was studied at preset time periods, of 7, 21, 28, 60, 120 and 180 days, using the following analytical setup. Diffraction analysis was performed in powder samples with a Siemens D-500 diffractometer (40KV/35mA). The spectra were collected between 5 ° and 50 ° 2θ scale, with a step of 0.03 ° / 5 s.

SEM examination was carried out in fractured surfaces, using a FEI Quanta Inspect scanning electron microscope, while DTA/TG was operated with a Perkin-Elmer Pyris 3000 Thermal Analyser. Samples were heated in static air atmosphere up to 1000 °C at a rate of 10 °C / min.

^{1}H NMR T_1 relaxometry measurements were acquired using a spectrometer with operating ^{1}H resonant frequency 12.1718 MHz coupled to a 0.29T benchtop permanent magnet. The sample was placed into NMR glass tubes and sealed with Parafilm®. All measurements were conducted at room temperature and the hydration process was followed for 2 months with time intervals from minutes to days.

Results

The T_1 distribution profiles showed two different peaks for T_1. The shift of the main peak is related to the development of the C-S-H phases. The second peak, which appears in later times (28 days), corresponds to the redistribution of water in the pore network, due to the decomposition of C-A-H phases. These observations are consistent with the XRD, DTA/DG and SEM data

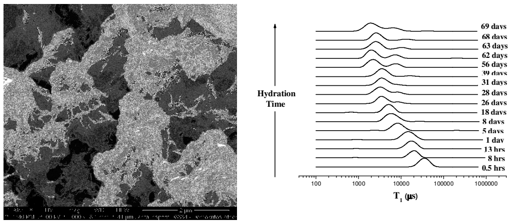

Figure 1: *SEM photomicrograph (left) exhibiting the development of hydrous gel around the pozzolan particles and; T_1 distribution profiles (right).*

Conclusions

^{1}H NMR was successfully applied, in combination with XRD, DTA/DG and SEM, to the study of the hydration process of lime-pozzolan mortars, providing information on the development of the hydration process and the resulted microstructure changes, The results indicate the great potential of ^{1}H NMR for studying both at laboratory and in field the monitoring of hydration and water content of lime-pozzolan mortars.

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VIBRATIONAL AND ESR SPECTROSCOPY USED TO STUDY PAPER PERMANENCE

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Introduction

Main factors of paper decay, a natural process, are UV-Vis radiation, temperature, humidity and biological attack [1]. A relative new conservation procedure of printed archives is gamma irradiation. Our goal is to establish a conservation procedure based on physical, chemical and microbiological tests before and after irradiation.

Experimental

Old books (Romanian and American) and newspapers (Romanian and Belgian) were analyzed before irradiation using spectral methods.

Bruker Vertex 70 class FT-IR spectrometer equipped with a fiber optic mobile RAMPROBE attached to RAM II module (LN2 Ge detector) was used. FT-Raman spectra were recorded between 50 and 3500 cm^{-1} using Nd:YAG laser (1064 nm, 1-500 mW). Spectral acquisition was made with 100 scans at a 4 cm^{-1} resolution. *In situ* measurements were made directly on the paper surface. FT-IR spectra were recorded in KBr pellets [1]. Vector normalization of the spectra on the whole frequency range was done.

For electron spin resonance (ESR) testing a Magnettech Miniscan MS200 X band spectrometer was used. Gain varied according to the signal intensity of the measured sample [2].

Results

FTIR results permit characterization of different aged books (Fig. 1a) discerning the presence of oxidized celluloses (see peak of 1727 cm^{-1}). Also for newspapers clearly different spectra are observed (Fig 1b). New Europe Journal spectrum resembles well with the cellulose spectrum whilst the Agenda spectrum presents intense absorptions at 1454 and 1430 cm^{-1} indicating more alcohol groups due to shorter cellulose chains. Raman spectra of American and Romanian books (Fig. 1c) show distinct peaks at 1600 cm^{-1} and 638 cm^{-1} probably due to different saturation degrees. A signal due to cellulose (g_{symm}=2,004) is observed in the ESR spectra of all samples. The intensity of signal is proportional with the quantity of cellulose free radicals present in the sample. Some newspapers contain also traces of Mn.

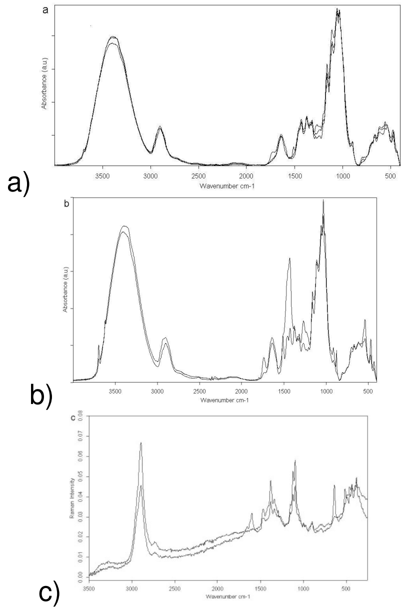

Figure 1: *a) FTIR spectra of first and middle page of 1962 and 1982 books; b) FTIR spectra of newspapers; c) FT-Raman spectra of American (1976) and Romanian (1962) books.*

Conclusions

The examination of spectral characteristics of paper samples furnishes indication about the decay process. Complementary FT-IR and Raman analysis provides information on cellulose derivatives paper components.

Acknowledgements
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NON-DESTRUCTIVE ANALYSIS AND IDENTIFICATION OF ANCIENT EGYPTIAN PIGMENTS

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Introduction

Polychromatic decorations of ancient Egyptians tombs and temples have a long tradition over three millennia. It has been demonstrated that the ancient color hues cannot be determined from present visual perceptions because many pigments have been subjected to severe chemical reactions, which have entirely changed their original colors. Pigments from various archeological sites in Egypt were analyzed: Optical microscopy, PIXE and microbeam-PIXE have been used for determination of the nature of pigments, their chronology, and identification of domestic and imported materials. Such a study is also important for conservation of mural paintings.

Experimental

Pigments of mural paintings from various archeological sites in Egypt like: Valley of the Kings, Al Minya, and Habu Town, etc, have been analyzed. All specimens were loose pieces of wall paintings collected on the spot in different tombs. They consisted of thick painted plaster.

Broad beam PIXE analysis with 1.0 MeV protons was performed at SINS, Warsaw using the Lech Van de Graff accelerator. Microbeam-PIXE analysis was performed at Institute of Ion Beam Physics and Materials Research, Forschungszentrum Dresden. Optical observations were carried out with Bosch Schott Optical Microscope in the Institute of Electronic Materials Technology.

Since ancient Egyptian pigments are limited to minerals and inorganic materials the complete chemical analysis is not indispensable for pigment identification. Instead the detection of a characteristic element, a fingerprint, is sufficient.

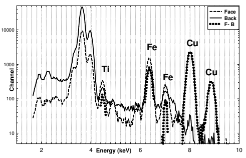
Results

From fig (1) one can notice the elements Si, Ca, Cu were identified as main elements of Egyptian Blue. Yellow sample shows Fe Iron Oxide Hydroxide α FeOOH and Spectra of PIXE analysis of red sample shows the elements Fe Iron Oxide Hydroxide Fe2O3.

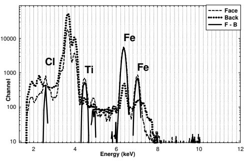
Conclusions

According to the optical microscopy observations paint is composed of grains of sizes typically ranging from 50 µm to 300 µm embedded in binding material. Optical microscopy revealed also great non-uniformity of pigment depth and lateral distributions and discontinuity of the paint layers. In some places paint flaked off and the supporting plaster become visible. This effect is due to the longtime exposure of wall paintings to environmental degradation factors. Preliminary analysis using broad beam PIXE has been performed allowed determination of the average composition of support and that of pigments. The microbeam PIXE has been used for mapping of selected grains. Important findings on the pigment composition of mural paintings at different archeological sites and interesting details of painting technique of ancient masters have been revealed

PIXE spectrum of blue sample. The presence of strong Si, Ca, Cu peaks identifies this pigment as Egyptian Blue.



PIXE spectrum of yellow sample. The presence of strong Fe peaks leads to the conclusion that the pigment is goethite.



PIXE spectrum of red sample. The presence of strong Fe peaks leads to the conclusion that the pigment is Hematite.

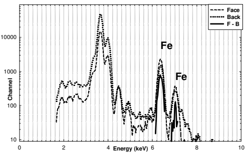


Figure 1 *The presence of strong Si, Ca, Cu peaks identifies this pigment as Egyptian Blue.*

The presence of strong Fe peaks leads to the conclusion that the pigment is goethite FeO OH.

The presence of strong Fe peaks identifies this pigment Hematite Fe_2O_3.

Acknowledgements

Sincere thanks are due to Ms. M. Mozdzonek (ITME) and Dr. B. Schmidt (FZD) for their help with optical microscopy.

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ON GOING STUDY OF TREATED AND NON-TREATED CORUNDUM SAMPLES

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Introduction

Detecting colouring-diffusion treatment for enhancement of corundum ($\alpha-Al_2O_3$) properties is a major concern for gemstone dealers and jewellers. This process involves heating the minerals while in contact with some flux and a berylium oxide source in the appropriate redox conditions.

Late studies of corundum treated samples have showed that the combination of PIXE, IBIL and µ-Raman allows discrimination between treated and non-treated corundum [1]. IBIL's potential for mineral characterization has been previously discussed [2].

The aim of this work is to corroborate that the discriminating methodology described in our previous work still applies to a set of new corundum samples, and refine the before mentioned methodology to be applied in the Cultural Heritage field for systematic analysis of minerals and gemstones.

Experimental

The analysed samples include 20 natural corundum minerals and other 21 treated either with some BeO source or with BeO and flux, coming from Umba (Africa) or of unknown origin.

All minerals have undergone PIXE and IBIL analysis at the IPNAS-CEA cyclotron of the University of Liege. Some representative samples have been selected for µ-Raman analysis to be performed at the Vakgroep Analystiche Chemie of the University of Ghent.

Set-up for all the techniques has been improved and new X-ray detector and spectrometers have been acquired.

Results

The examination of the treated and non-treated corundum samples showed systematically the presence of phosphorous, often used in the form of phosphates as flux. Results of on going IBIL and µ–Raman analyses, will too be presented.

Conclusions

The study of this large number of treated and non-treated corundum adds to our previous experience, thus contributing to establish a non-invasive and non-destructive analytical protocol that includes the use of some complementary techniques, useful both in the field of material sciences and Cultural Heritage.

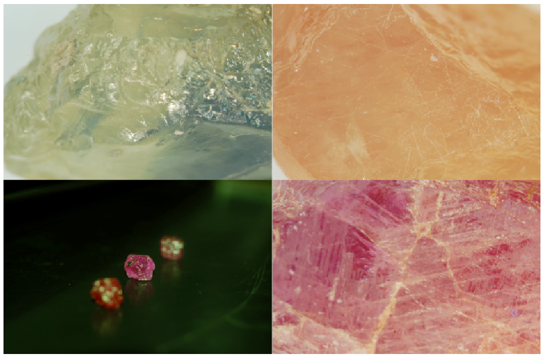

Figure 1: *Images of some corundum samples analysed in this work*

Acknowledgements

The authors would like to acknowledge Antonio Negueruela S.A. for providing the corundum samples for this work. Also technicians A. Marchal, M. Philippe, A. Holsbeek, M. Clar and S. Rakkaa.

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THE STUDY OF ARCHAEOLOGICALLY INTERESTING GLASSY AND METAL ARTEFACTS IN HAS-ATOMKI

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The Laboratory of Ion Beam Applications of ATOMKI is based on a 5 MV Van de Graaff (VdG) electrostatic accelerator equipped with an RF ion source. The available ions for analysis are as follows: H^+, D^+, $^4He^+$ within the energy range of 1-3.8 MeV. We are specializing in non-destructive elemental analysis with a milli- and micrometre size ion beam.

The ATOMKI-IBA staffs have two decades of experience in the field of application of ion beam methods. The research activities are focused on joint studies with Hungarian Museums (Hungarian National Museum, Budapest History Museum, Debrecen Museums) as well as with foreign institutions: CNRS (Centre Ernest Babelon, Orléans, and Laboratoire de Recherche des Musées de France, Paris), CNA (Centro Nacional de Aceleradores), Seville, and Departamento de Prehistoria, Instituto de Historia, Madrid.

In this paper ion beam applications in art and archaeology are presented. Concerning metals, a result on silver coins will be cited, and a work on some bronze artefacts of the Tumulus culture in the Danube-Tisza region (Middle to Late Bronze Ages) will shortly be discussed. From the former and current work on the ion beam analysis of glassy materials those will be shown, where beside the PIXE also the PIGE technique played role. These are the followings: to find subgroups among the classified obsidian sources of the Tokaj Mountains (Hungary), the investigation of classical ring-stones and their imitations and the study of glassware from the Middle Ages in Hungary.

COMPARATIVE STUDY OF OLD MORTARS FROM EVORA AND ELVAS CATHEDRALS (SOUTHERN PORTUGAL)

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Introduction

The study of old mortars, based on integrated methodologies that combine mineralogical, microstructural, chemical, physical and mechanical characterization has an important role on the preservation of architectonical cultural heritage, allowing a deep knowledge about the materials used, construction techniques, possible repairs and behavior [1,2]. The production of mortars depended on the availability of raw materials and hence the mineralogical composition is especially relevant to establish direct correlation between provenance and use. This study on the two cathedrals (Elvas and Evora) underlined the importance of local resources as main source of aggregates. The raw materials for the production of lime seem to be related to trade routes rather than local provenance. The use of specific materials reflects the technological capabilities and developments of the society that built the Cathedrals.

Experimental

This work focus on the mortars mineralogical composition in what concerns to aggregates, binder and neoformation compounds.

Several samples were taken from different walls of the cathedrals under supervision of IPPAR (Portuguese Institute of Architectural Heritage) technicians. After a drying period, each specimen was disaggregated and split into several fractions to be used by different techniques. Stereozoom and petrographic microscopes were used to identify the mineralogy and morphology of the aggregates and study the textural properties of each mortar. X-ray diffraction was preformed to allow a further insight on the mineralogy of the binder and aggregates. A Philips X'Pert difractometer with Co Kα radiation, step of 0.05 °/s, between 2θ 3° and 74 ° was used. The thermo analytical techniques gave additional information on the composition of the binder. A Setaram TG200 equipment was operated under argon atmosphere and uniform heating rate of 10 °/min from room temperature to 1000 ºC.

Results

By stereozoom microscope, it was possible to identify the most important aggregates like quartz, feldspars, micas and amphiboles. The presence of ceramics was also evident in some samples and has extreme importance since the addition of this material was a technological way of improving the mechanical quality of the material. The petrographic microscopy improved the capability to identify optically the aggregates and allowed the recognition of minerals typical from the geological environment of Elvas and Évora.

XRD showed that some mortars are mainly calcitic whereas others have magnesium carbonates (dolomite and hydromagnesite). These results were corroborated by TG-DTG which showed typical endothermic peaks characteristic of thermal decomposition of these carbonate specimens.

Conclusions

This work shows that in the two studied Cathedrals, the aggregates are sands from the region and reveal the local geology. The relative abundance of each mineral component of the aggregates reflects its natural regional abundance and the resistance to weathering processes. The lime manufacture shows a greater selectivity of raw materials and the use of magnesium carbonates on the mortar from later construction periods which can be interpreted as a technological advance from medieval times.

Acknowledgements

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GILDING MATERIALS AND TECHNIQUES USED IN ERUDITE AND POPULAR PORTUGUESE POLICHROME BAROQUE WOODEN SCULPTURES

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Introduction

Very little is known about the materials and techniques used in Portuguese polychrome wooden sculpture from the Baroque, although it had great symbolic importance in this period. The published studies based on a scientific approach are scarce and, although a detailed review already exists, it is still very limited, since it was based on a small number of cases [1]. Among other aspects, the technical differences between pieces that can be classified as erudite or popular remain undiscussed. More specifically it is not known if the artistic features of each group, mainly related to the wood carving quality, are followed by the use of different materials and techniques in the polychrome layers that coat the wooden support. Here we address this issue in relation to the use of gold leaf, a material extensively employed in polychrome Baroque sculptures, particularly for the representation of brocades and other rich textiles. The effects were mainly obtained through the *estofado* technique, which involved the application of paint layers over the gold leaf and its scraping off before the paint is completely dry, revealing the gold beneath according to a certain pattern.

Experimental

Seven sculptures (Table 1), four with erudite features E1-E4) and three with popular ones (P1-P3), were studied. They have been made in Northern Portugal during the last quarter of the 17th century and the first half of the 18th century and undertaken conservation treatment in the School of Arts of The Portuguese Catholic University, in Oporto. The identification of the materials and characterization of the techniques used in the polychrome layers were made through in situ analysis by non invasive energy dispersive X-ray spectrometry (EDXRF) and through analysis of microsamples by optical microscopy (OM), polarized light microscopy (PLM), scanning electron microscopy equipped with an energy dispersive X-ray spectrometer (SEM-EDS), Fourier transform infrared spectroscopy (FTIR) and microchemical tests [2-4].

Results

The gold leaf was identified in the areas of *estofado* and, in some pieces, also in some attributes and base. The gold was applied over a layer of natural bole, a fine clay with high content of iron compounds. The bole was applied over a ground layer mainly composed of calcium sulphate. This corresponds to the expected sequence when water gilding is used, as it is the case of all pieces. The gold is partially covered by one or more paint layers. In general, the gold leaf was applied in the entire area of the garments, that is, both where the *estofado* technique was used and where the garments do not show any decoration. However, in two erudite pieces the rear side of the garments has gold leaf only in areas of *estofado* (E2, E4). In one erudite (E1) and the three popular sculptures the *estofado* technique was not employed at all at the rear side, as the gold was not used there. Besides, in one of the popular pieces (P2) the use of gold at the front side was limited to the area of *estofado*. In average, the gold content of gold leaves used in erudite sculptures is 87.7% (Table 1). Although in one popular piece a similar value was also found (P1), in the others (P2, P3) the gold content is significantly lower.

Table 1: *Sculptures and composition of the gold leaf*

Sculptures		**Gold leaf composition**		
Code	**Subject**	**Au/%**	**Ag/%**	**Cu/%**
E1	Saint Dominic	84.4	6.3	9.3
E2	Saint Francis Xavier	88.5	5.9	5.6
E3	Saint Paul Martyr	82.9	7.6	9.6
E4	Saint Andrew	95	-	-
P1	Saint Stephen	88	6	4
P2	Virgin of the Annunciation	77.2	16.3	6.5
P3	Saint John Evangelist	75.4	16.9	7.6

Conclusions

Regarding the use of gold leaf, some significant differences between erudite and popular pieces were found. In popular sculptures some measures that can be related to cost reduction were adopted: the gilded area was particularly minimized and gold leaves with small gold content were employed.

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CHARACTERIZATION OF GOLD LEAF FROM A BAROQUE ALTARPIECE

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Introduction

There are several studies concerning the investigation of the Portuguese altarpieces from the baroque period, regarding national or regional productions. These researches are mainly focused on the typological, social, economic and religious aspects surrounding the construction of these altarpieces. Concerning the study of the materials and techniques applied, the approach is mainly based on documents analysis such has treatises and orders from the manufacturing period. Some of these documents have references to the materials used (gold, pigments, varnishes) and where and how they were applied [1] [2]. Even though the study of this art works has numerous references, there is still a gap concerning a direct study, only focused on the gold leaf and the technology involving its application. The present work aims to provide a new approach to the study of the Portuguese baroque altarpieces, by grouping the existing information regarding both compositional and textural aspects that are directly related to the production of the gold leaf. In a final and broader approach to this investigation it will be possible to define the provenance and circulation of the gold applied in the different Portuguese baroque altarpieces.

Experimental

The analysed samples were taken from the main altarpiece of San Francisco church in Porto, which is one of the most emblematic churches from the baroque period in Portugal. The samples were selected from discrete but a representative area in the main altarpiece such has the back of the columns or the step of the throne. Several exams were performed such has scanning electronic microscopy with an energy dispersive X-ray fluorescence (SEM-EDS) (Hitachi SU-70, equipped with micro-analysis by X-ray (EDS-WDS), 55 kV, mag. 300 and by a minimum period of 60 seconds) and optical observation of cross-sections by polarizing transmitted optical microscopy (Zeiss Stemi 2000-C, with external artificial light system Zeiss KL 1500 LCD, image acquisition with digital camera AxioCam MRcS and an Axio Vs 40 V4.4 Carl Zeiss Vision GmbH acquisition and treatment software).

Results / Conclusions

The cross section analysis showed a typical gilded surface stratigraphy, with three main layers: ground layer, *bollus* and gold leaf (Fig. 1). The results from SEM-EDS revealed the presence of a gold-silver-copper alloy and by further spectrum analysis of the weight per cent concentrations it was possible to identify a 23 karat gold using also a ternary diagram [3]. The figure 2 illustrates the surface of the gold leaf and the scanned area. The presence of other elements such has iron, silicon, aluminium; magnesium, calcium and sulphur are typical of the *bolus* and the ground layer.

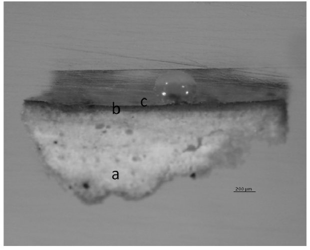

Figure 1: *Cross-section: a) ground layer; b) bollus; c) gold leaf.*

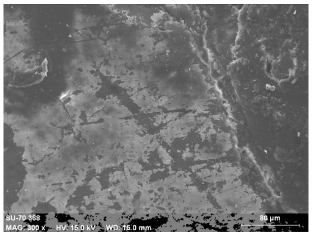

Figure 2: *Surface of the scanned gold leaf by SEM-EDS.*

Acknowledgements

Foundation for Science and Technology (FCT), for PhD scholarship SFRH/BD/38593/2007.

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X-RAY CAPILLARY OPTICS: DEVELOPMENT STATUS

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Introduction

Modern development in capillary optics is directed to a decrease of focal spot sizes and an increase of brilliance. Such parameters can be realised if corresponding high brilliant microfocus sources are available and a high quality of the capillary optic is guaranteed [1]. Furthermore, capillary optics can be used for quite different X-ray analytical methods. For these applications an optimisation of the optic for the required energy interval is necessary. In this contribution an attempt was made to realise extremely small focal spot sizes. This objective may be achieved by using high brilliant microfocus X-ray sources in combination with compact polycapillary lenses. But instruments in which optical elements are used, do not allow the realisation of an optimal geometry in all cases. In the considered instrument the possible minimum distance between the anode spot and the sample was much larger than the optimal distance. Therefore, an important task will be the realisation of a small focal spot independent of the source-sample distance. To achieve such a result several technological and physical problems must be solved.

Furthermore, examples for a flexible optimisation of an optic for a defined energy band are required. This can be influenced by a variation of the capillary sizes [2].

Experimental and results

For obtaining small focal spots at large source-sample distances several polycapillary lenses were manufactured and characterised. One of these lenses has a distance of about 400 mm between both foci and will be used for XRF application in scanning electron microscopes /.iMOXS../. In this case a focal spot size smaller than 30 µm was realised in a broad energy interval. With another lens focal spot sizes below 15 µm were achieved. Furthermore, a lens was especially designed for a high efficiency in the low energy region 1 – 5 keV. This lens should allow an efficient excitation of the lines of the L-series of In and the K series of S and Na. As a result minimum detection limits better than 1 % are achieved for these elements.

Conclusions

It was shown that a polycapillary optic may be flexible adapted to a concrete application. Here geometrical parameters as well as spectral characteristics may be varied.

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X-RAY CAPILLARY OPTICS: NEW APPLICATIONS

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Introduction

Meanwhile the possibility to control efficiently X-ray radiation using modern capillary systems allows their application in a variety of different analytical methods [1,2]. These applications concern also new objects such as thin layers and samples of small volumes. For example, in the manufacturing technology of multilayer systems, which are used as absorbers, a permanent control of elemental composition and thicknesses of the layers is necessary. Furthermore, information about the phase composition and its depth distribution in the layer is required. If additionally a 2-dimensional detector is used in such a XRD-setup, the measurement time could be decreased dramatically and advanced insights in crystallite size changes, texture effects are possible. In this contribution an attempt was made to solve these problems.

Experimental and results

Using of strongly focussing polycapillary lens systems in XRD and XRF set-ups spot sizes down to the 10µm range are realised and measurement times in the range of a few seconds are possible. Using such a polycapillary optic in combination with laboratory X-ray sources diffractograms with local resolution are obtained. Also depth resolved XRF and XRD measurements are realised. X-ray tubes with an anode spot of 50 µm in size and a power consumption of 30 W and an X-ray tube with a rotating anode with a spot size of about 100 µm and a power consumption of 2 kW were used as sources. For focussing X-radiation polycapillary lenses are manufactured which realise focal spots of a maximum brilliance. A special geometry of the outcoming beam, which realises an additional collimation using a slit, allows not only XRF measurements but also diffractometry with an angular resolution. A geometry like this also allows the realisation of glancing incidence angles of the primary radiation. This is important for a separate measurement of secondary signals from different sample depths. In the present contribution another method of separation of the emission of secondary radiation from different depth regions is realised: the registration of secondary radiation under small exit angles. In this way angular dependencies of XRF and XRD signals are measured. It was shown that the XRF and XRD yield curve are different for different materials corresponding to its depth distribution in the layer.

Conclusions

In the present contribution several examples of new applications for capillary optics in XRF and XRD are given. These applications concern for example the characterisation of graded thin layer systems of modern photovoltaic elements.

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MULTILAYERS QUANTITATIVE X-RAY FLUORESCENCE ANALYSIS

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Introduction

X-Ray Fluorescence spectrometry (XRF) allows a rapid and simple determination of the elemental composition of a material. As a non destructive tool, it has been extensively used for analysis in art and archeology since the early 1970's. Whereas it is commonly used for qualitative anaysis, recent efforts have been made to develop quantitative analysis even with portable systems. However the interpretation of the results obtained with this technique can turn out to be problematic in the case of layered structures such as easel paintings. The use of differential X-Ray attenuation can allow to model the various layers: indeed the absorption of x-rays through different layers will result in modification of intensity ratio between the different characteristic lines.

This work focuses on the possibility to use the software PyMca [1], developed at the European Synchrotron Radiation Facility, to reconstruct layers composition and thicknesses.

Our method was tested on several multilayers standards. Then as an example of *in situ* application a painting from Marco d'Oggiono, pupil of Leonardo da Vinci, was studied.

Experimental

The XRF spectra were acquired with a portable system designed and constructed in the C2RMF laboratory. This system uses a tube with Ag anode, and a solid state Si(Li) AXAS-V detector. A helium flux allows the detection of elements down to sodium. X-ray spectra were analyzed by the dedicated software PyMca, with the Fundamental Parameter Method.

The standards used were very thin metallic and polymer layers superimposed. Various thicknesses of Kapton were laid on a lead plate to model a varnish layer applied on a white lead based painting layer. A test painting was also prepared by a restorer according to the 16th century recipes [2] and analysed.

Results

Results obtained on the standards confirmed the accuracy of the method. Figure 1 presents the result obtained for various thicknesses of organic layers, compared to the certified values.

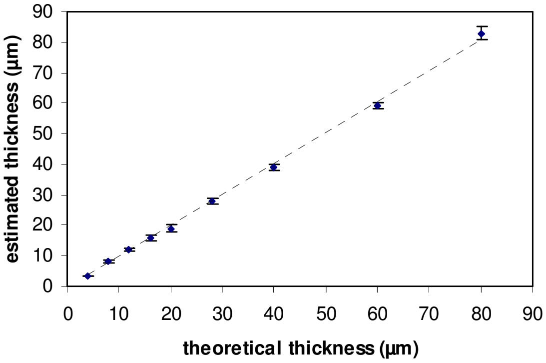

Figure 1: *XRF analysis on polymer layers laid on a thick lead plate: comparison between the certified and the estimated thicknesses with PyMca treatment.*

A maximum error of 5% on the calculated thickness was obtained for thicknesses above 5µm. Under 5µm thickness, the error do not higher 0,5µm.

Varnish measurements on the panel "The Holy Family" from Marco d'Oggiono indicated values between 25 and 35µm depending on the analysed zones. An interesting result is also the increase of the organic layer thickness in the darkest part of the carnations. This would indicate the use of glazes to model the shadows [2].

Conclusions

We thus demonstrate the possibility to do quantitative XRF analysis in multilayers structures by the use of PyMca software. This method provides valuable results for the thickness and the composition of the different layers.

For painting analyses, a very fast and accurate varnish thickness measurement can be obtained. A more complete study of paint layers will be more complex as it necesitates a good modelisation and thus a great knowledge of the technique used.

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DETECTION OF DEGRADATION ORIGIN IN CARBONATE MATERIAL BY ISOTOPIC AND MINERALOGICAL TECHNIQUES

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Introduction

This study was conducted in order to determine the causes of degradation of the material by a 13th century hagiography. The hagiography was made on a porolithe wall of a small church, which collapsed during an earthquake in 1981. During restoration, the porolithe was scraped and let clear from the outer crust. After restoration works, weathering phenomena were observed on the hagiography which ended up to the degradation and collapse of its material.

Aiming to the detection and determination of the degradation observed in the hagiography, samples were analyzed using stable isotopes of carbonates (^{13}C, ^{18}O) and XRD analysis.

Experimental

Twelve samples from the structural material of the hagiography were analysed. The samples were taken from the healthy surface of the material as well as from the weathered and the collapsed part. Salts precipitated by water were also sampled. XRD analysis was applied to identify the mineralogical structure of each material. The isotopic measurements (δ^{13}C, δ^{18}O) were used to determine the origin of the carbonate material. The isotopic analyses took place in the Stable Isotope Unit of Institute of Materials Science (NCSR Demokritos) on a Thermo Delta V Plus IRMS equipped with GasBenchII.

Results

XRD analysis indicated that the samples are mainly carbonate materials, consisted of calcite, dolomite and aragonite. However, the participation of sulphate minerals in all samples shows sulphation of the original carbonate material. Other minerals detected were quartz, gaitite, albite and orthoclase.

Isotopic signatures of the samples range between -9,5 to -19,5‰ for δ^{13}C and -9,6 to -16,8‰ for δ^{18}O. Especially, the isotopic values of ^{18}O indicate that the weathering was caused by water intrusion which diluted and recrystallized the carbonate material.

Conclusions

The final results of the study indicate the type of the degradation of the hagiography material. In general, the sulphation of carbonates is obvious. The main cause of this sulphation is probably chemical degradation by acid rain. The isotopic composition suggests that water penetrates the original material which goes through weathering and re-precipitation phenomena.

Table 1. *XRD analysis of samples*

Sample	Minerals
AL-1	Calcite, Aragonite
AL-2	Quartz, Calcite, Albite
AL-3	Calcite, Dolomite, Aragonite
AL-4a	Calcite, Aragonite
AL-4b	Kaolinite, Calcite, Quartz
AL-5	Calcite, Anhydrite
AL-6a	Calcite, Dolomite
AL-6b	Calcite, Dolomite
AL-6c	Calcite, Dolomite
AL-7a	Calcite, Quartz
AL-7b	Quartz, Calcite
AL-8	Calcite, Dolomite, Quartz

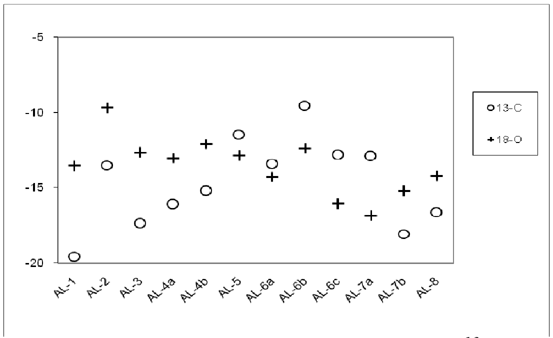

Figure 1: *Isotopic composition of samples (δ^{13}C and δ^{18}O vs PDB ‰)*

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DETERMINATION OF THE ORIGIN OF CARBONATE MATERIAL FROM ANCIENT TESSERAE BY ISOTOPIC AND MINERALOGICAL TECHNIQUES

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Introduction

For the characterization and the identification of the origin of tesserae from the Palace of Galerius, Thessaloniki, Greece, samples were analyzed using several techniques: stable isotopes of carbonates (^{13}C, ^{18}O), XRD analysis and optical microscopy, from which information can be obtained on the origin and texture of the material used for the production of the artifacts.

Experimental

The analysed samples are 22 archaeological tesserae pieces. XRD analysis was applied to identify the mineralogical structure of each material. Based on that, the isotopic measurements (δ^{13}C, δ^{18}O) were used to determine the origin of the carbonate material. The isotopic analyses took place in the Stable Isotope Unit of Institute of Materials Science (NCSR Demokritos) on a Thermo Delta V Plus IRMS equipped with GasBenchII. In order to distinguish the material of the tesserae in more detail, the maximum grain size of each was determine by optical microscopy.

Results

The tesserae have different colours, which is natural and depend on the source of rock used. XRD analysis indicated that most samples are carbonate rocks, mainly consisted of calcite, with dolomite and quartz participation in some cases. A few tesserae seem to be made by metamorphic rocks. Isotopic signatures of the tesserae range between 0,35-2,94‰ for δ^{13}C and -4,1 to -2,65‰ for δ^{18}O. Detailed determination of the origin of each material was achieved using the maximum grain size (MGS).

Conclusions

The final results of the study indicate the origin of the material of the tesserae from Galerius Palace. The origin of most samples was determined, as the data plotted well on known ancient quarries. However, some samples were not similar materials with the known quarries and therefore it is concluded that they were made by stone from unknown locations of quarrying.

Table 1. *XRD analysis of samples*

Sample	Minerals
D-01a	Dolomite
D-01b	Dolomite
D-02a	Calcite, Quartz
D-02b	Calcite, Quartz
D-03a	Antigorite, Montrmorillonite
D-03b	Antigorite, Chrysotile
D-04a	Calcite
D-04b	Calcite, Dolomite
D-05a	Calcite, Quartz
D-05b	Calcite, Quartz
D-06a	Calcite, Dolomite
D-06b	Calcite, Dolomite
D-07a	Calcite
D-07b	Calcite
D-08a	Calcite
D-08b	Calcite
D-09a	Calcite
D-09b	Calcite
D-10a	Calcite
D-10b	Calcite, Quartz, Dolomite
D-11a	Calcite, Quartz
D-11b	Calcite, Quartz, Anorthite

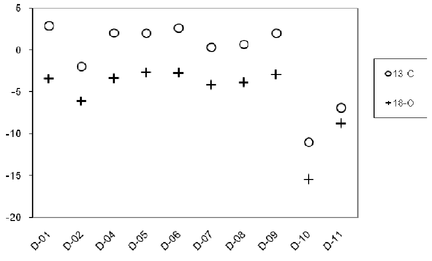

Figure 1: *Isotopic composition of samples (δ^{13}C and δ^{18}O vs PDB ‰)*

MICROANALYTICAL INVESTIGATION OF PIGMENTS AND PLASTERS OF WALL PAINTINGS FROM BYZANTINE CHURCHES IN MANI (GREECE)

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Introduction

The present study concerns wall paintings from a series of Byzantine churches in Mani, a sparsely populated peninsula in Southeast Peloponnesus (Greece). Written sources from the Byzantine era in general offer only scarce detailed information about painting techniques [1]. In this context, the churches in Mani provide an interesting case study, presenting construction phases from different historical periods, from the 10th to 13th century. The monuments are located in a relatively limited area and some of the wall paintings were created presumably by the same artists or workshops. The study, furthermore, was expected to provide information about possible differences between local and metropolitan monuments in the Byzantine Empire, which were subject of comparable studies [2].

Experimental

In order to examine the entire stratigraphy of paint layers applied on the plaster, it was necessary to take small samples from the wall paintings. A total of 32 samples was collected from 12 different churches. Sections of the samples were prepared and imbedded in resin. The sections were ground and polished in order to be examined first under the optical microscope. Afterwards, the sections were carbon-coated to be examined under the scanning electron microscope (SEM). The SEM was used in combination with energy dispersive X-ray spectrometry (SEM-EDS) in order to determine the chemical composition of pigments, binding materials and plaster. For investigation of the mineralogical composition of the plaster, selected samples were powdered and examined with X-ray diffraction (XRD).

Results

The adherence of the paint layers to the preparatory layer indicates that the ‘fresco a secco’ technique was applied for the construction of the wall-paintings. In most cases the used pigments were soil based materials, ochre but also fine clay without particularly high iron oxide content and maybe terra verte. For dark colours usually powdered charcoal was used. Only in some cases the use of other pigments such as cinnabar, minium and lapis lazuli could be confirmed. Furthermore, there might be the possibility that hornblende was used as a kind of dark pigment. The preparatory layer of the wall paintings consists of a thin lime mortar layer. The coherence of this layer ranges from a very compact with pores size bellow 50 µm to a loose microstructure with a considerable amount of micro-cracks. In many cases particles of non-hydrated lime (CaO) are identified, which are indicative for a local and pressing production.

The high magnesium concentrations in some of the samples are noticeable particularly at the surfaces. This could be due to the use of dolomitic plaster as binder or due to the use of magnesium rich pigments. There is also the possibility that the wall paintings were covered at some point with a different, i.e. more dolomitic, plaster.

Conclusions

The analytical results demonstrate a relatively high level of artistic techniques in a remote and rather rural area of the Byzantine Empire, using at least to some extent similarly precious pigments as in metropolitan monuments.

Acknowledgements

The analytical work was part of a project on Byzantine wall paintings coordinated by M. Panayotidi and S. Kalopissi-Verti at the University of Athens, which has been funded by EPEAK II/ PYTHAGORAS II

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THE GARMENT OF A BYZANTINE EMPEROR FROM MOUNT ATHOS: OBSERVATION & ANALYSIS USING SEM-EDS

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Introduction

Ecclesiastical textiles of the post-Byzantine period have been scarcely fully studied, despite the relatively large and impressive collections of garments which is spread around the numerous Christian Orthodox monasteries around the world. Very limited information is available for these precious textile artefacts of the eastern Euro-Mediterranean cultural heritage. Their origin, construction materials and stage of preservation is usually not well documented or originated and therefore questionable.

This poster is focussed on a garment which, according to tradition, belongs to the Byzantine Emperor Ioannis Tsimiskis (925-976) and is displayed in Iveron monastery in Mount Athos. It represents the culmination of a detailed survey from the most important monastic centre of the Orthodox Christianity, the 'Holy Mountain' of Athos. Today, Mount Athos has an outstanding universal value, according to the UNESCO, as it houses rich collections of artworks from various chronological periods.

Experimental

Combination of optical microscopy and microstructural analysis such as SEM- EDS is employed for the observation of the surface morphology and the qualitative analysis of the metal threads of one of the most important garment (*sakkos*) of Mount Athos. Hence a series of cross-sections were collected and examined.

Two samples were taken from already damaged areas. The examined metal threads derive from embroidering on the ground fabric and not from supplementary elements, such as sequins or other decorative elements.

Results

The metal threads of the *sakkos* are solid wires laid couched on the ground fabric following the Byzantine and post-Byzantine construction techniques that remained unchanged until nowadays.

Based on the Optical Microscopy the samples appear to be silver in terms of colour and shininess. In general, the preservation state appears to be in a fair condition without heavy deposits or corrosion products (Fig. 1). No significance differences between the outer and inner part of the metal threads was be observed. In the cross-sections the mass of the metal is homogenous therefore no gilding could be identified. Scratches, decay and loss of the metal were also observed on the samples, which could possibly allow further deterioration to take place through electrochemical processes.

Conclusions

SEM is a widely used method for compound analysis and can help in the conservation field by raising awareness to the profession and promoting further opportunities for analysis of more Athonian textiles with similar methods. This technique is used to support the historical analysis but also to give valuable information before or after any preventive or interventive treatment of these garments.

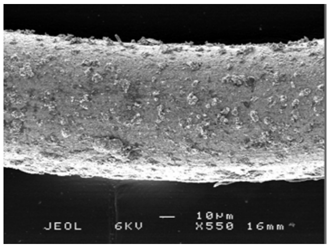

Figure 1: *SEM view of the wire thread (magn. 550x)*

Acknowledgements

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ANALYTICAL STUDY OF THE PAINTING 'EDUCATION OF CUPID' ATTRIBUTED TO CORREGGIO: PRELIMINARY RESULTS

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Introduction

The painting 'Education of Cupid' attributed to Correggio, entered the collection of the National Gallery, Athens in 1900. Since the early days, many assumptions were made on the provenance of the painting and the identity of the painter by several experts in the field. Between 1936 and 1939, in an attempt to provide some answers, the conservator Georgios Stratigos carried out a major intervention to remove the extensive overpainting. Almost seventy years on most of the questions remain still open. The present study aims at documenting the current preservation state of the painting, characterising the materials and the technique used for its preparation, and identifying the layers of overpainting. Moreover, an overview is given of the known paintings with the same subject, attributed or not to Correggio, that are found in other collections, including the National Gallery in London, with as much information as could be collected on them.

Experimental

Following optical observation and UV-VIS-IR electron imaging of the painting surface, a number of samples was collected. Selected cases were prepared in cross sections and their stratigraphy recorded under the analytical microscope. The organic compounds were characterised using the technique of gas chromatography (GC-FID), while for the inorganic materials scanning microscopy – energy dispersive X-ray spectroscopy (SEM-EDX) was employed.

Results

In the samples analysed, several pigments were identified, amongst which lead white, carbon black, green earth and led-tin yellow. A drying oil was also detected that has been used as a binder. All the above are paintings materials that have been extensively employed in Western European painting.

Conclusions

In its present state the lined painting has numerous losses that are covered with overpainting. The preliminary results of this study can potentially become the spur to further research and comparative studies with some of these paintings, including those attributed to Correggio. Furthermore, a list was drawn up of seventeen (17) paintings of the same subject, most of them found today in various European collections. Another ten (10) paintings have been sold by various fine art auctioneers.

Figure 1: *'Educaton of Cupid': IR reflectance image (950-1150 nm) of a detail*

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STUDY OF SLOTS AND GROOVES CORROSION PHENOMENA IN HELLENISTIC GLASS BEADS

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Introduction

Corrosion of glass has been studying extensively for over 40 years now. Silicate glasses corrode by two main mechanisms: leaching and network dissolution. Although the corrosion mechanism has been the thoroughly studied, the corrosion morphology of excavated glasses has not been the included in many research projects. Corrosion morphology of excavated glass varies with the most common phenomena being dulling, iridescence, translucent to opaque whitish surface, blackened external corrosion layers and/or crusted surface. "Spontaneous cracking" is a rare phenomenon reported for different types of transparent glass (Medieval painted glass, Roman vessels etc.). In effect the term comprises to at least three different phenomena, namely feather-cracks, lenticular fractures and slots or grooves. All of them are attributed to a damaged surface, which has undergone corrosion or weathering [1-3]. However, slots or grooves have also been detected on opaque archaeological glass used for the main body or for decoration.

The present work aims to study the formation of slots and grooves detected on translucent and opaque glass beads of Helllenistic period.

Experimental

Macroscopic and microscopic examination of Hellenistic beads condition revealed the presence of an extensive network of grooves and/or slots on opaque white and yellowish glasses, as well as on heavily altered translucent green glasses. Polished cross sections of representative samples were examined under optical and scanning electron microscope, coupled with EDX (SEM/EDX) in order to study the microstructure and the compositional changes of corroded glass.

Results

The network of shallow grooves or deeper slots detected on translucent and opaque glass beads do not extend right through the thickness of the bead, like the ones reported for transparent glass vessels. Macroscopic and microscopic examination of beads surface differentiates the grooves from slots by their width and mainly by the presence or not of corrosion layers on their sides.

Optical microscopy and SEM examination of slots revealed the presence of a solid substance in their core. Compositional data about the solid core indicates the accumulation of Pb and Sb related to the opacifier and colourant, combined with an enrichment of other elements (P, Ca, Cl, Fe, Mn), due to glass alteration.

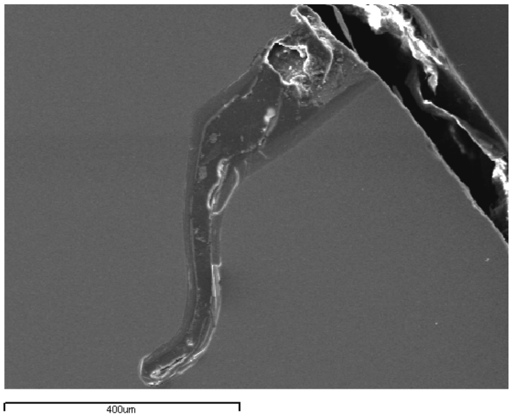

Figure 1: *Detail of a "groove" on the glass body in cross section.*

Conclusions

The study of slots and grooves revealed information about their nature and offered an additional indication for the formation of slots on opaque glasses.

Acknowledgements

The authors would like to thank Dr. P. Triantafyllidis (KB΄Archaeological Ephorate of the Dodecanese, Greece) for the opportunity to study the glass finds and for his collaboration.

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EVALUATION OF EFFECTIVENESS OF TANNED LEATHER CLEANING WITH SEM-EDX AND FTIR SPECTROSCOPY

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Introduction

Leather has been traditionally used in various everyday applications and art objects since antiquity. Industrial processes such as the various types of tanning have increased the applicability of this material. However, it is still considered as one of the most sensitive materials towards environmental hazards, hard use, etc. Techniques for leather cleaning involve the use of various solvents, soaps and detergents, surface dry-cleaners, etc. Most of the research work done so far on the use of these media aimed basically at the effectiveness of leather surface cleaning. The present work aims at a spectroscopic (FTIR, FTIR-microscopy and SEM-EDX) evaluation of the possible effects of various cleaning procedures on leather as a result of physical/chemical interaction of the medium with the protein material, as well as with any added compounds present.

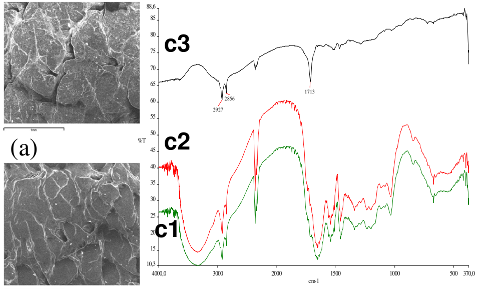
Experimental

An FTIR spectrometer (PE Spectrum GX) was used for the analysis of KBr tablets of powdered samples scraped directly from the leather surface. A PE AutoImage FTIR microscopy accessory, coupled to the basic unit (reflectance mode), was used in the case of cross-sections and surface detection. SEM was used (Jeol JSM-5310 with a Link Pentafet detector) on graphitized leather samples. Tanned goat leather samples (approx. 2×1 cm) were used in all cases, with no further aging process.

Results and Discussion

Leather samples were cleaned in one part, leaving almost half of the surface in a non-cleaned state for comparison purposes. Cleaning media used: solvents (white spirit, trichloroethane, acetone, alcohol-water mixture), acidic and alkaline media (hydrochloric acid, aqueous ammonia solution), water-based detergents (Texapon®, Synperonic N®), a hydro-carbon-based detergent (Vulpex® in white spirit) and a natural rubber-based surface dry-cleaner (Groomstick®).

FTIR spectra (KBr samples and microscopy) were examined comparatively between adjacent cleaned and non-cleaned areas on each of the tested leather samples. A small shift in the expected amide I vibration was detected in all ono-cleaned samples, along with the detection of small amounts of tannin, ester-type compounds (presumably, oils) and ketone carbonyls. In the cleaned samples, the most notable changes were observed in the case of acetone, ammonia solution and ethanol-water (reduction of esters and protein-related components), trichloroethane (reduction of protein-related components), and Vulpex® in white spirit (reduction of hydrocarbon chains and ketones, see Figure 1).



(a) (b) (c)

Figure 1: Leather cleaned with Vulpex®/white spirit: SEM image (a) before, and (b) after cleaning; (c) FTIR spectra before (c1) and after cleaning (c2) and the resulting difference spectrum (c3).

Analysis of cleaned leather surface, with SEM-EDX showed significant increase of Cl for hydrochloric acid - cleaned surface, Na for Texapon® and K for Vulpex®. Finally, small increase of S, K, Ca and Si and appearance (low levels) of Na, Si and Cl was detected in the case of Groomstick®.

Conclusions

FTIR spectroscopy and SEM-EDX were employed to investigate the alterations on the surface of tanned goat skin induced by a number of cleaning media. Detergent in non-polar solvent (white spirit) and solutions of extreme pH values (HCl and NH_3) have been found to cause chemical alterations on components of leather surface.

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PIGMENTS CHARACTERISATION OF 14TH CENTURY WALL PAINTINGS FROM BANJSKA MONASTERY IN SERBIA

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Introduction

In this work several wall paintings' colors from the Banjska Monastery (Saint Stephan), in Serbia, were examined for the identification of pigments components and materials, as well as for the investigation of pigments' preservation state. Banjska Monastery was constructed from 1312 to 1316, under the order of the Serbian King Milutin, who intended to use it as his Mausoleum. Even though, Banjska Monastery was luxuriant decorated, comparing to other monasteries that Milutin ordered their construction and was also their granter, no inscriptions are preserved to indicate the artist(s) who performed the iconographies. Therefore, further aim of the authors is to compare, in future works, colour materials and techniques used in Banjska Monastery with the colour materials and techniques used in the wall paintings of other churches and monasteries in Serbia that Milutin ordered and funded their construction. This comparison of materials and techniques would be of particular interest in the cases of those monasteries where it is well established that the famous artists Michael Astrapas and Eutychios were employed by King Milutin for the iconography making.

Experimental

The identification of pigments took place on samples with colors of red, violet and yellow. The analysis of the pigments was carried out using the following techniques: Fiber Optics Microscopy (FOM), Chromatometry, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS), X-ray Diffraction (XRD), and Micro FT Raman.

Results

The analysis by the techniques used indicated that the examined red colour is consisted of cinnabar, hematite and minium, where the ground layer is red ochre; the yellow colour is consisted of yellow ochre, whereas violet colour is either caput mortuum, or caput mortuum with cinnabar and carbon black. Even though, the colour layers were generally in good preservation state, they displayed some localised flaking and detachments, while red colour presented some localised discolouration, attributed to minium pigment chemical alteration.

Conclusions

All the identified pigments belong to the traditionally used natural pigments of the Byzantine iconography in the 14th century. Although the name(s) of the artist(s) who performed the wall paintings in Banjska Monastery is not preserved, it is concluded that he/they performed with noteworthy artistic technique the wall paintings of the Mausoleum of King Milutin. Further research though is necessary in order to examine more colours of the wall paintings of Banjska Monastery, as well as, to ascertain the technique(s) used for the structure of the colour layers. Then, a comparative study among wall paintings' colour and techniques of the same era would be possible to be achieved.

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STUDYING AN UNCOMMON GILT LEATHER - THE CASE OF THE CONVENT OF THE ORDER OF CHRIST OF TOMAR (PORTUGAL)

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Introduction

The Convent of the Order of Christ of Tomar is one of Portugal´s most important historical and artistic monument and was classified as World Heritage by UNESCO, in 1983. The original Convent was built in the 12th century and since then it has suffered numerous interventions and amplifications, particularly in the 15th and 16th centuries that rendered the convent its actual appearance.

The Charola of the Convent presents a great diversity of techniques and materials [1], including a few specimens of gilt leather.

Gilt leather is an uncommon technique in Portugal and the majority dates from the 18th century. This is a decorative technique that combines gilding, painting and engraving on a leather support [2]. Besides the gilt nomination, in fact, the leather applied on stone walls is covered by a silver plate with a finishing layer of a yellowish varnish [3].

The aim of this work is the characterization of the materials used in the Charola's gilt leather technique and its stratigraphic structure.

Experimental

Different areas of the gilt leather were sampled as microfragments and mounted on epoxy resin in order to expose its stratigraphy. The cross-sections were assessed by Optical Microscopy and Scanning Electron Microscopy coupled with an Energy Dispersive Spectrometer (SEM-EDS).

The different layers were also characterized by Fourier Transform Infrared µ-spectrometry (µ-FTIR), optical microscopy and µ-chemical analysis. The metals of the gilt leather were also analyzed by X-ray fluorescence µ-spectrometry (µ-XRF) and the superficial varnish was identified by µ-FTIR.

Results

The combined analysis of the referred techniques revealed three types of metal foils covering the leather namely tin, silver and gold.

Stratigraphic analysis showed examples of the original technique (using a silver foil), false gilt leather (with a tin foil) and a gold foil. The last one corresponds, in fact, to the common gilding technique, with a subjacent *bolus* layer. The gilding with gold foil is historically unusual on leather supports, and in this case it was found on the top of the false gilt leather.

The support's leather nature was only confirmed by SEM-EDS micro-structural analysis, due to its state of conservation.

Conclusions

The gilt leathers found in the Charola of Tomar are probably the most antique known in Portugal and still remain in the original place. During the restorations, the original support was maintained, and different gilding techniques and paint layers were applied.

Acknowledgements

The authors wish to thank to IGESPAR and CIMPOR for the restoration financial support and to Nova Conservação Lda. And EEA Grants for financing the scientific investigation.

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CHARACTERIZATION OF OLD-STYLED THAI GOLD MOSAIC GLASS USING ELECTRON MICROSCOPY AND X-RAY MICROANALYSIS

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Introduction

Gold mosaic glass has been used as decorate art since ancient times, first in Spain and Greece and then in the whole Mediterranean. In Thailand, the gold mosaic glass that brought from foreign is used to decorate on the old-styled Buddhist sites, such as temples and sanctuary. This glass is degrading overtime, thus restoration works can be of urgent necessarily. As a result, understanding the glass's chemical composition and phase constitution is a must in conservation and restoration process.

Modern techniques for materials characterization are going increasing usage in the area of archaeological materials science, especially the application of electron probe microanalysis (EPMA) for the study of the materials used in early glass production, and electron microscopy and x-ray microanalysis for characterization the microstructure of opaque colored glass mosaics from mediaeval church [1,2]. There is some previous works in Thailand to study and analyze the Ancient Thai Glass samples using scanning electron microscopy (SEM) and X- ray fluorescence spectroscopy (XRF) [3]. In this study, the application of SEM/EDX is used to characterize the microstructure of gold mosaic glass samples from a Buddhist sanctuary in Bangkok, Thailand.

Experimental

The gold mosaic glass samples to be studied were small fragments, flat, and about 2 mm thick selected from a Buddhist sanctuary. Optical microscope was used to study a macrostructure of these samples. The microstructural investigation of the gold mosaic glass samples were carried out using SEM/EDX. Samples were coated with a thin layer of gold prior to observation.

Results

Using optical microscope resulted the glass structure is divided into three layers, i.e., cover glass, gold layer, and glass substrate (Fig. 1). The glass-gold interfaces are of primary interest. From SEM/EDX revealed that the main compositions of the glass samples were Si, Na, and Ca.

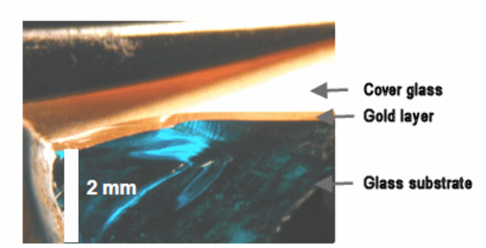

Figure 1: *Optical macrograph of the old-styled Thai gold mosaic glass sample*

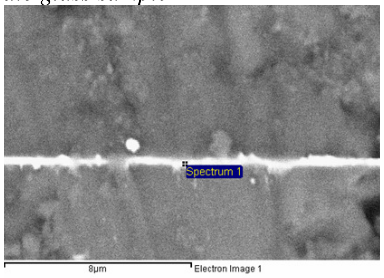

Figure 2: *SEM micrograph of the old-styled Thai gold mosaic glass sample*

Conclusions

It can be concluded that the old-styled Thai gold mosaic glass was alkali-lime silicate glass. The advanced studied found that the newly ones were successfully fabricated using a gold-foil coating technique on colorless glass prepared from Thailand resources.

Acknowledgements

The faculty of Science at both Kasetsart University and Chiang Mai University provided instruments for property measurements.

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DETERMINING OF ARTISTIC PAINT ORIGINALITY OF FAMOUS SERBIAN ARTIST SAVA SUMANOVIC USING FT-IR, SEM/EDS AND ICP-MS METHODS

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Introduction

Object of this analysis is the paint from the picture for who is suspected that is forgery of picture famous Serbian artist Sava Sumanovic. At the bottom right corner of the forgery picture is signature of Sava Sumanovic. Fig. 1.

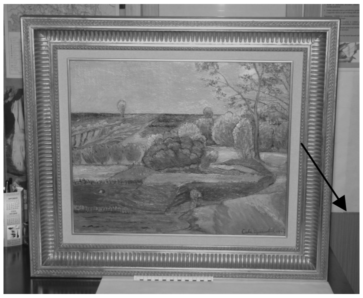

***Figure. 1**: Forgery picture of Sava Sumanovic*

It was noticed that forgery picture has been restored because there is a visible place where is the canvas glued on the new canvas that is impregnated using wax, like look of new little nails at the sideward part of the picture.

Uncontested samples white and black color are sampled at the Gallery Matica Srpska in Novi Sad from original pictures of Sava Sumanovic at the places which are mostly correspond to places where is sampled paint at the forgery picture.

Studying Gallery archives materials, the statement is that all paints which used by Sava Sumanovic has zinc-white, cobalt, chrome, cadmium and lead. In that time there were a lot of leads in white color, but later it was disabled, because of his very toxic features (reference is given by conservator), and it is equivalent to the result of the analysis.

Experiment

By the requirement of physical-chemical analyses there are used next metods: IR spectrophotometry (FT-IR), using brand instrument “Thermo Electron Corporation” type “Nexus 6700”, ATR techniques; Scanning Electron Microscopy with X-ray microanalysis (SEM/EDS) using instrument type JSM (Joel Scaning Microscope Low Vaccuum) model 6460 LV and method Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using instrument type Perkin Elmer model ELAN 5000.

Result

Using results of analyses of composite black paint by FT-IR spectrograms, there are determined that wave numbers of chemical functional groups of black paint sampled from contested paint didn’t match wave numbers of chemical functional groups black paint sampled from original paints.

Using results of analyses of composite white paint by FT-IR spectrograms, there are determined that wave numbers of chemical functional groups of white paint sampled from contested paint didn’t match wave numbers of chemical functional groups white paint sampled from original paints.

Analyzing derived data SEM diagrams of black and white paint configuration respectively, there is determined that uncontested sample of black paint contents 18 different Chemical elements, whereas contested sample contents 8 different elements. It`s identical for white paint.

Conclusion

Using foregoing laboratory methods, against differences in microelementary configuration, it has been confirmed that is investigated artistic paint of famous Serbian artist Sava Sumanovic, had been forgered.

Reference

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AUTHOR INDEX

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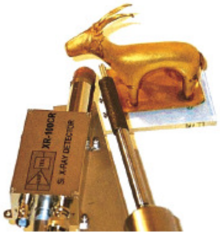

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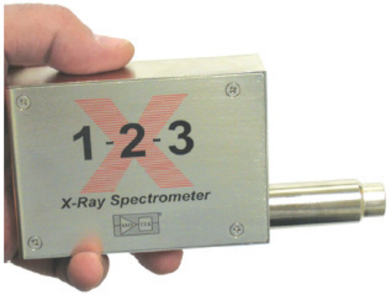
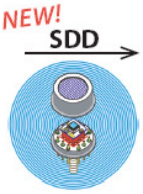
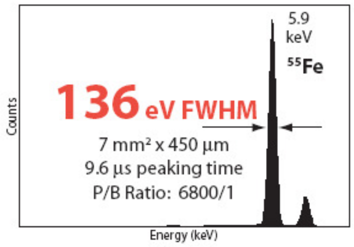
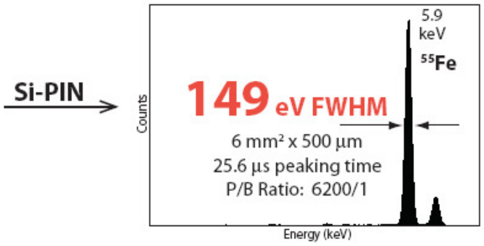


***PROVEN* PERFORMANCE**







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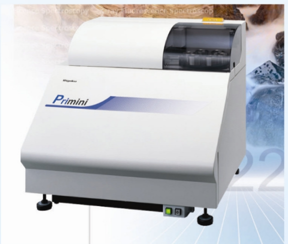
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